

Carbon Nanotube Activities at NASA-Johnson Space Center

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Abstract

Research activities on carbon nanotubes at NASA-Johnson Space Center include production, purification, characterization and their applications for human space flight. In-situ diagnostics during nanotube production by laser oven process include collection of spatial and temporal data of passive emission and laser induced fluorescence from C₂, C₃ and Nickel atoms in the plume [1]. Details of the results from the “parametric study” of the pulsed laser ablation process indicate the effect of production parameters including temperature, buffer gas, flow rate, pressure, and laser fluence [2]. Improvement of the purity by a variety of steps in the purification process is monitored by characterization techniques including SEM, TEM, Raman, UV-VIS-NIR and TGA. A recently established NASA-JSC protocol [3] for SWCNT characterization is undergoing revision with feedback from nanotube community. Efforts at JSC over the past five years in composites have centered on structural polymer/nanotube systems. Recent activities broadened this focus to multifunctional materials, supercapacitors, fuel cells, regenerable CO₂ absorbers, electromagnetic shielding, radiation dosimetry and thermal management systems of interest for human space flight. Preliminary tests indicate improvement of performance in most of these applications because of the large surface area as well as high electrical and thermal conductivity exhibited by SWCNTs.

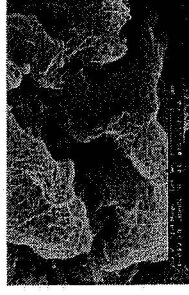
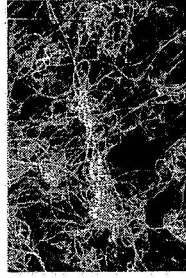
References:

- 1) Carl. D. Scott, Sivaram Arepalli, Pavel Nikolaev and R. E. Smalley, “Growth Mechanisms for Single-wall Carbon Nanotubes in a Laser Ablation Process”, *Applied Physics A*, Vol. 72, May 2001, pp. 573-580 (2001)
- 2) Arepalli S., Holmes W. A., Nikolaev P., Hadjiev V. G., and Scott C. D., “A Parametric Study of Single-Wall Carbon Nanotube Growth by Laser Ablation”, *J. Nanosci and Nanotech.* Vol. 4, 737-747 (2004).
- 3) Arepalli S., Nikolaev P., Gorelik O., Hadjiev V. G., Holmes W. A., Files B. S., and Yowell L., “Protocol for the Characterization of Single-Wall Carbon Nanotube Material Quality”, *Carbon*, Vol. 42, p. 1783-1791 (2004).

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Carbon Nanotube Activities at NASA- Johnson Space Center



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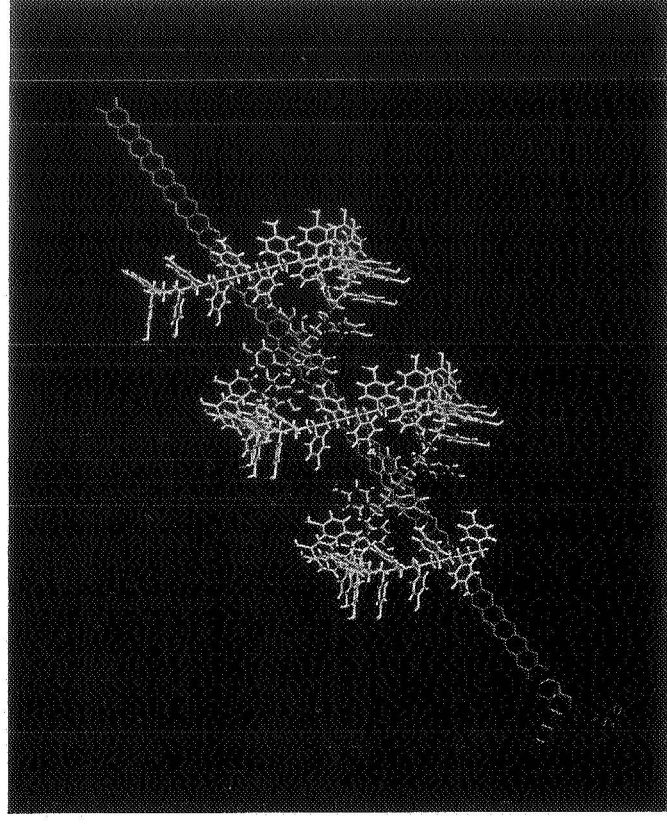
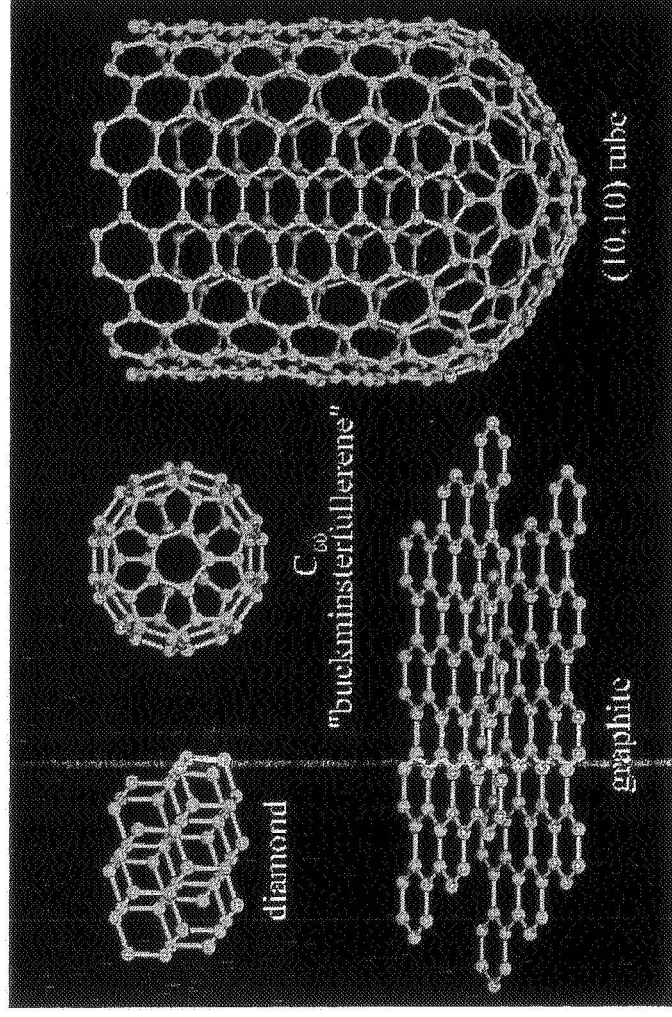
April 29, 2005



What are Carbon Nanotubes ?

Allotropes of Carbon—Graphite, Diamond, C_{60} , C_{million}

Nanotubes— Multiwall and Single wall (MWNT and SWNT)



Properties

Mechanical—handle large strains

Electrical—Metallic, semiconducting

Thermal— Anisotropic conduction

Misc.--Electron emission and large surface area

New Organic chemistry with this new form of Chemistry

Functional Groups attached to ends or sides to modify and enhance the SWNT properties and host matrices

Possibility of Nanosensors and multifunctional materials



Why Single Wall Carbon Nanotubes?

Mechanical Properties

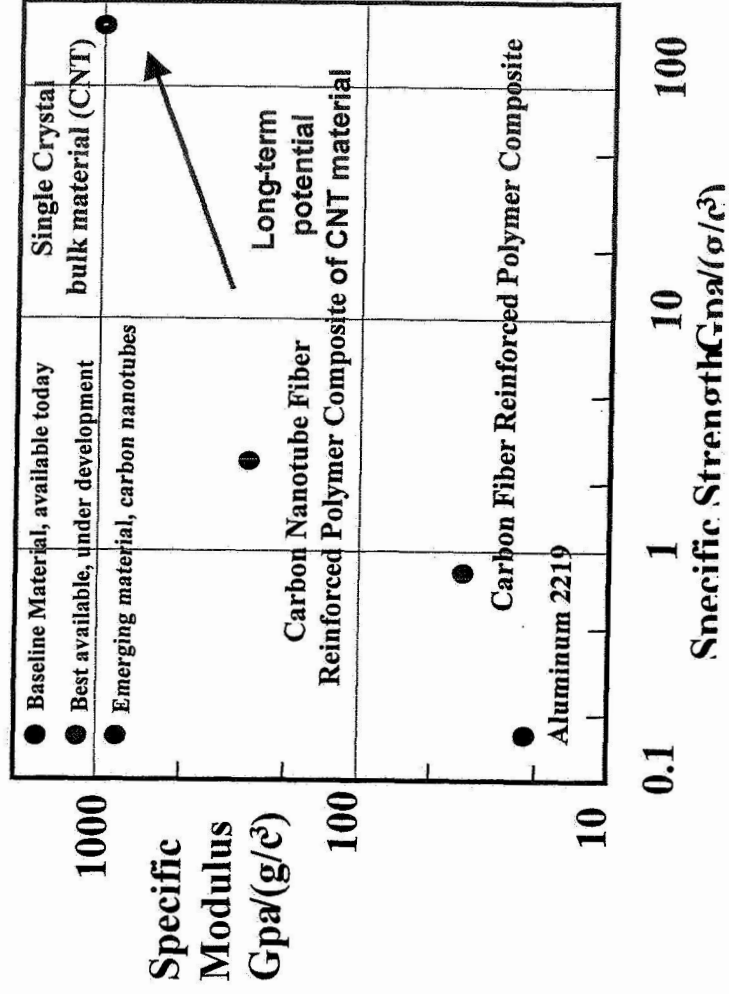
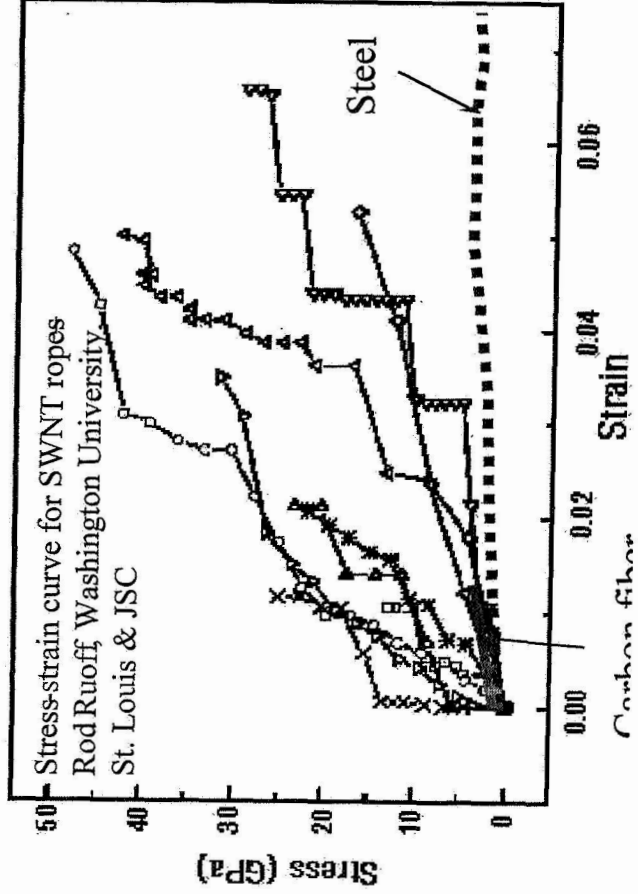
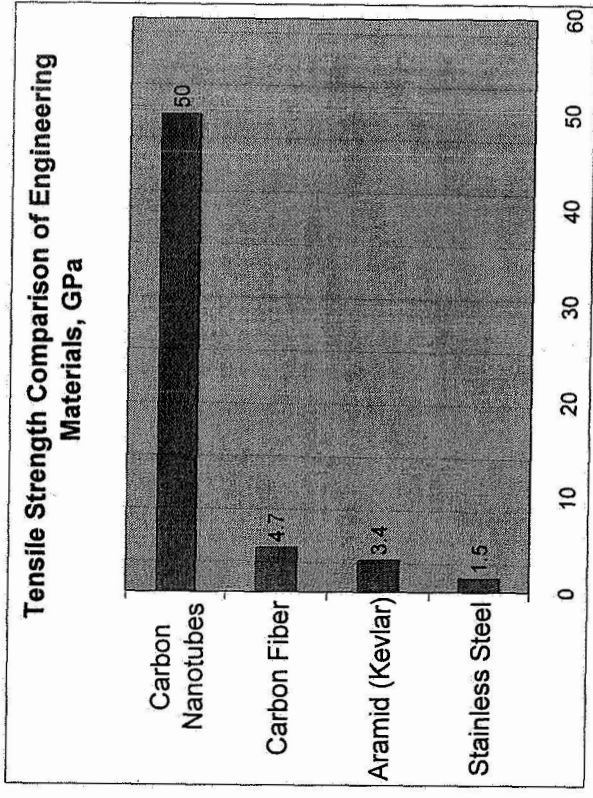
- much stronger/lighter than steel

Thermal Properties

- high longitudinal conductivity (diamond)
- low transverse conductivity (G_0)

Electrical Properties

- metallic, semiconducting tubes
- high conductivity (copper)





NASA Nanotechnology Roadmap

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Nanotube Technology Development Areas

Six Key Areas for NASA

- **Nanotube Production**
 - **NASA is currently funding a multi-year program of nanotube materials production and development at Rice University. However, numerous fundamental nanotube materials production needs were identified in this Roadmap, and the Rice Program should be tied to these needs.**
- **Modeling & Simulation**
- **Nanotube-based Materials**
- **Structural Applications**
- **Biological and Medical Applications**
- **Electronic & Mechanical Devices, Sensors, and Computing**

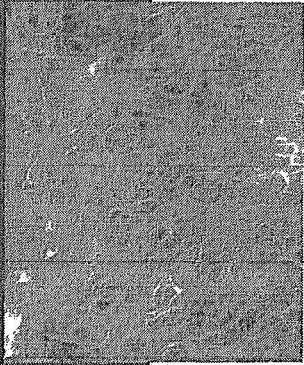


JSC Nanotube Group Activities

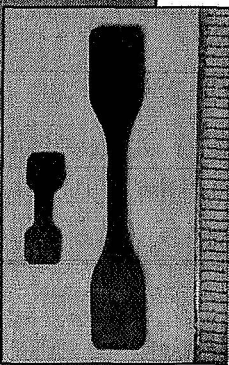
1 Make targets for laser process from graphite powder and metal nitrates



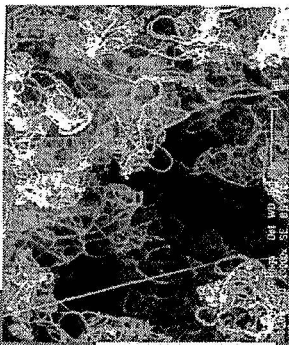
3 Nanotube purification



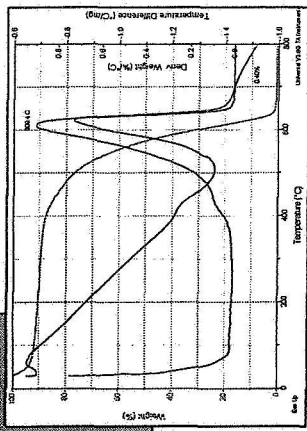
5 Composite fabrication



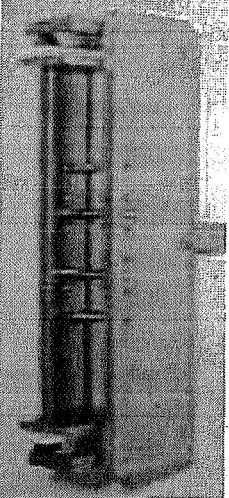
2 Produce single-wall nanotubes using laser and arc processes



4 Nanotube characterization for purity, length, diameter



6 Composite testing and analysis





NASA-JSC Nanotube Project Progress Details

- **Production and Growth Mechanisms**

- Production parameter study completed with variations in lasers, flow and furnace conditions
 - Importance of inner tube and sequencing of lasers
- Photodissociation study of C_{60} : Source of excited state C_2
 - Chem. Phys. Lett. Vol. 320, pp. 26-34 (March 2000)
- Growth mechanism study for laser ablation: Catalyst particles condense slower than carbon and carbon clusters break to provide additional carbon feed stock
 - Applied Physics A, Vol. 72, pp. 573-580 (May 2001)
- Production of Isolated Individual SWNTs: Long lengths
 - Applied Physics Letters, Vol. 78, pp. 1610-1612 (March 2001)

SWNT Growth Mechanism Workshop



JSC Nanotube Project Progress Details(Contd.)

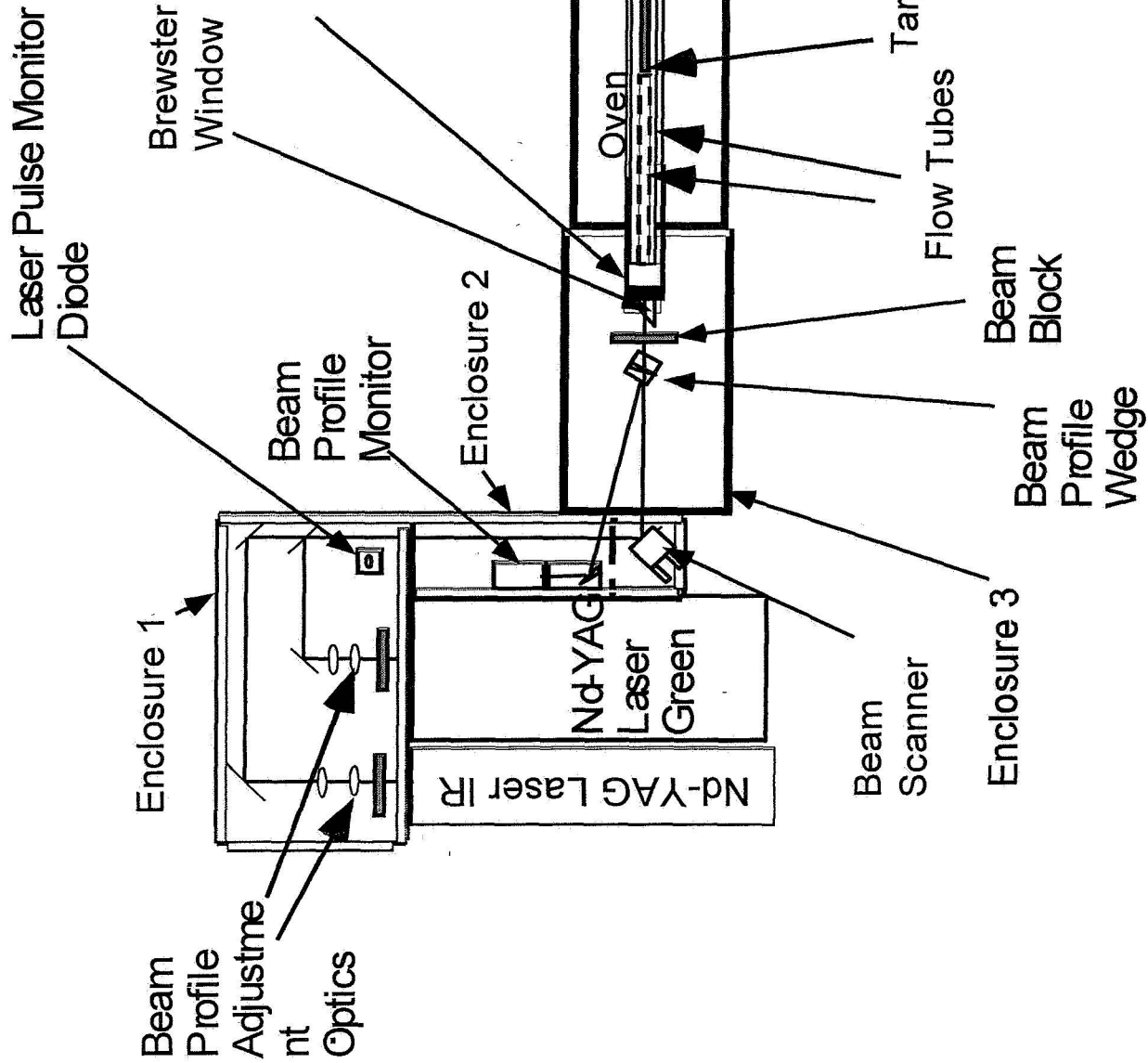
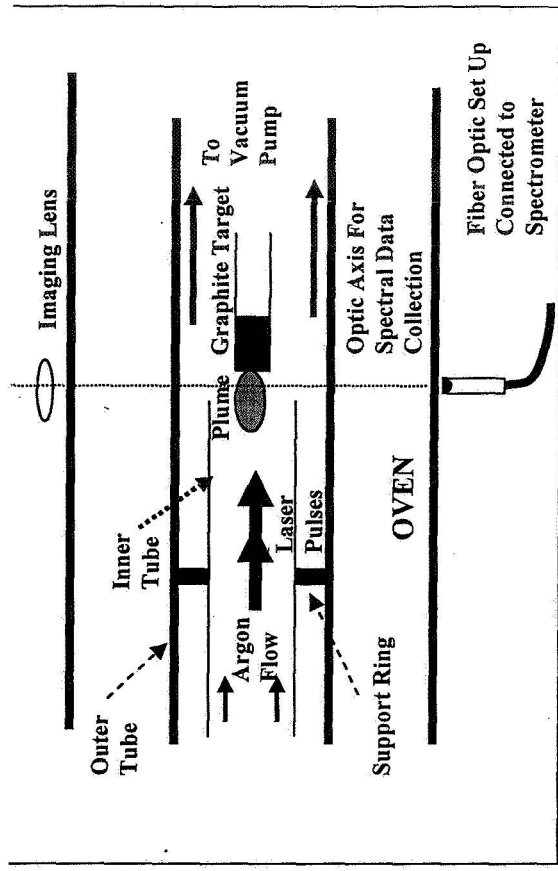
- **SWNT Purification and Characterization**
 - Completed part 1 of the purification procedures
 - NASA Contractor Report, NASA CR-208926
(May 2001)
 - Completed a preliminary study of surface energy measurements for SWNTs during different stages of purification
 - Established protocols for purification of laser and HiPco materials as well as characterization of SWNT using TGA, SEM, TEM, Raman and UV-VIS
 - Trying to become a reliable source of SWNTs

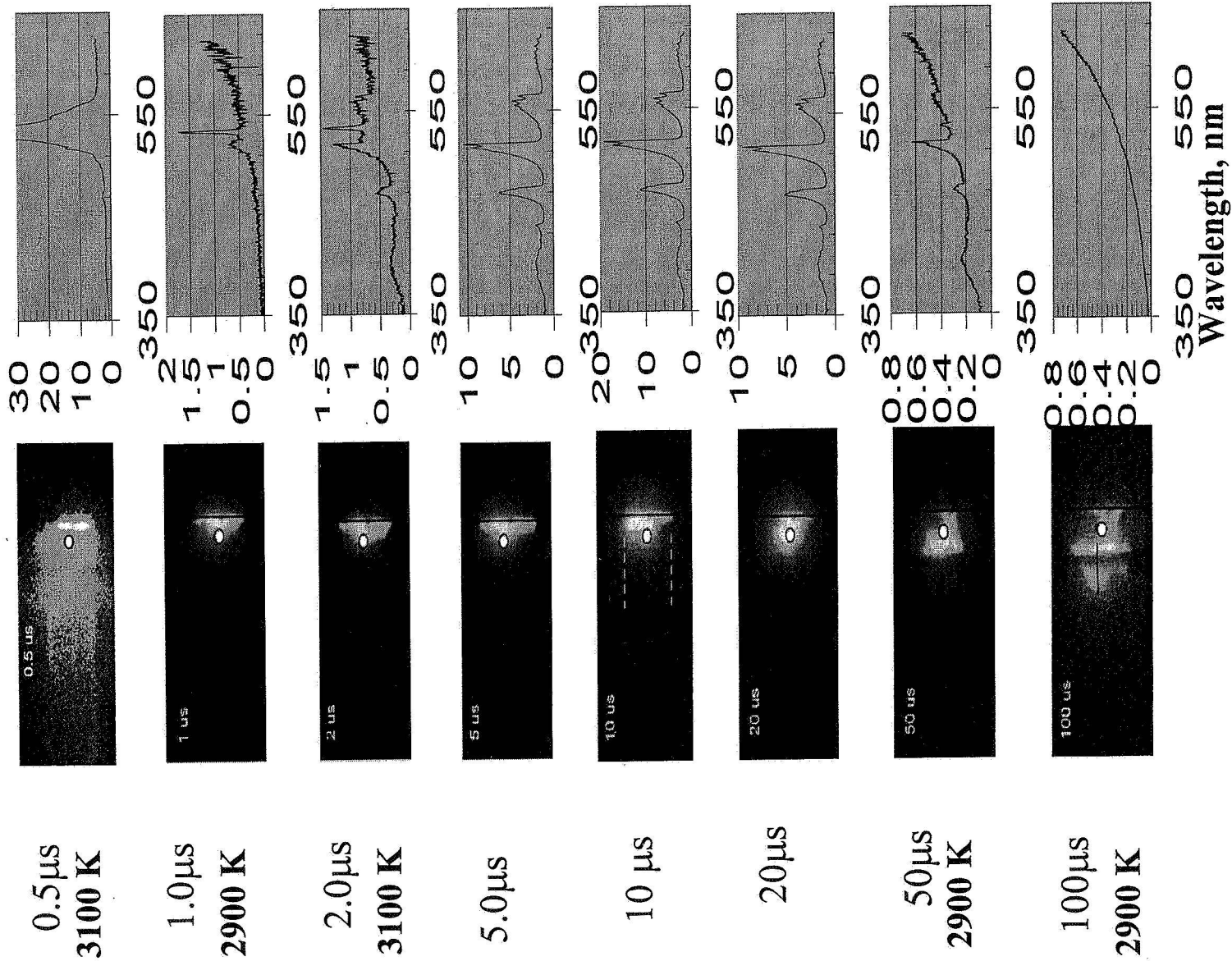
NASA/NIST Joint Workshop on Characterization

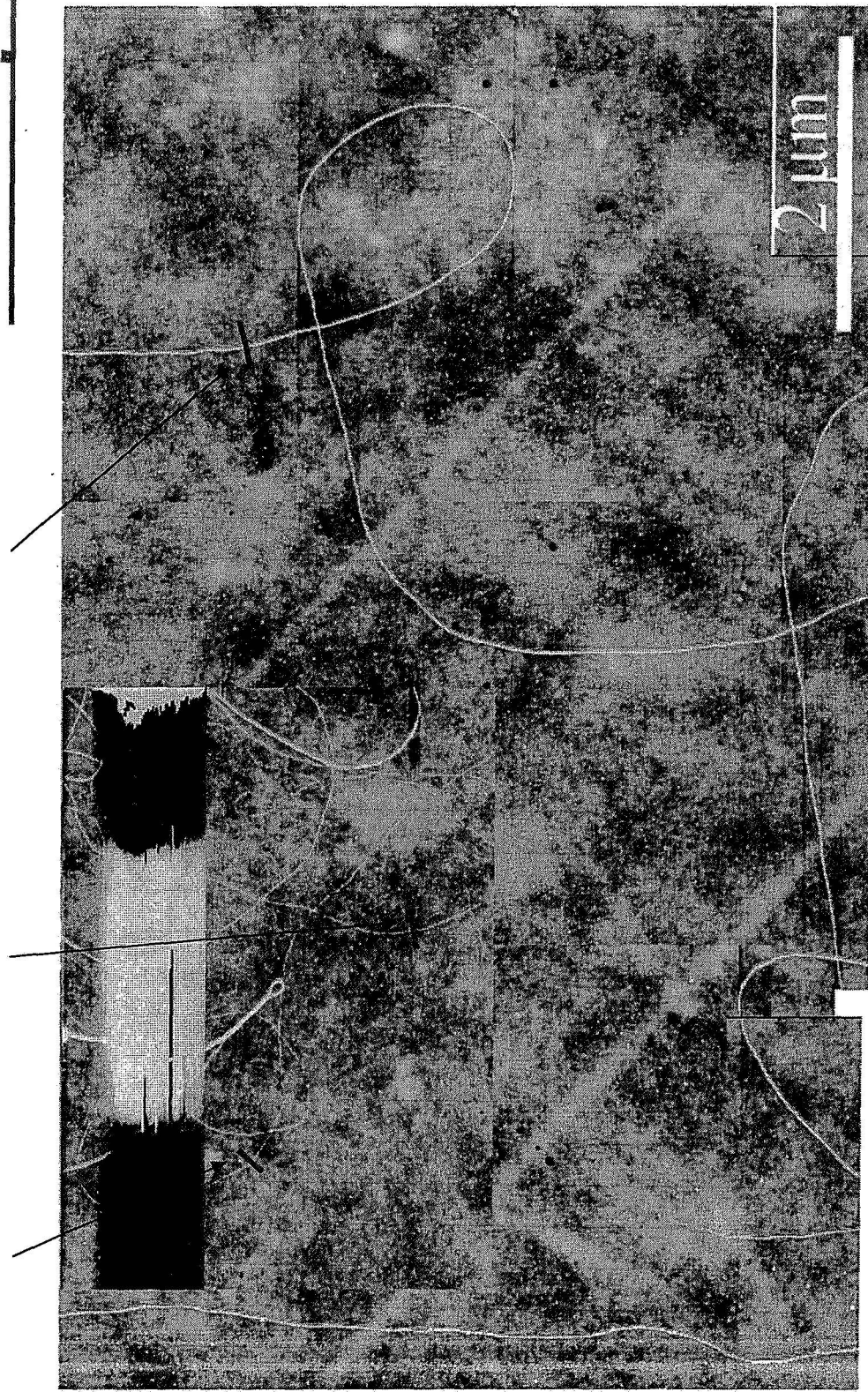
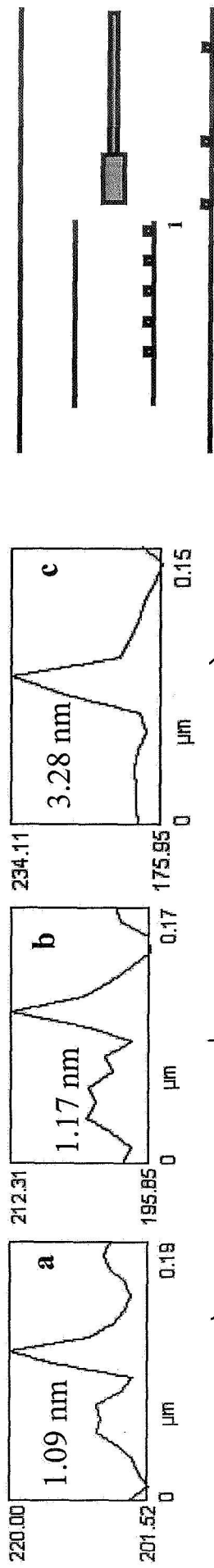


JSC Nanotube Project Progress Details(Contd.)

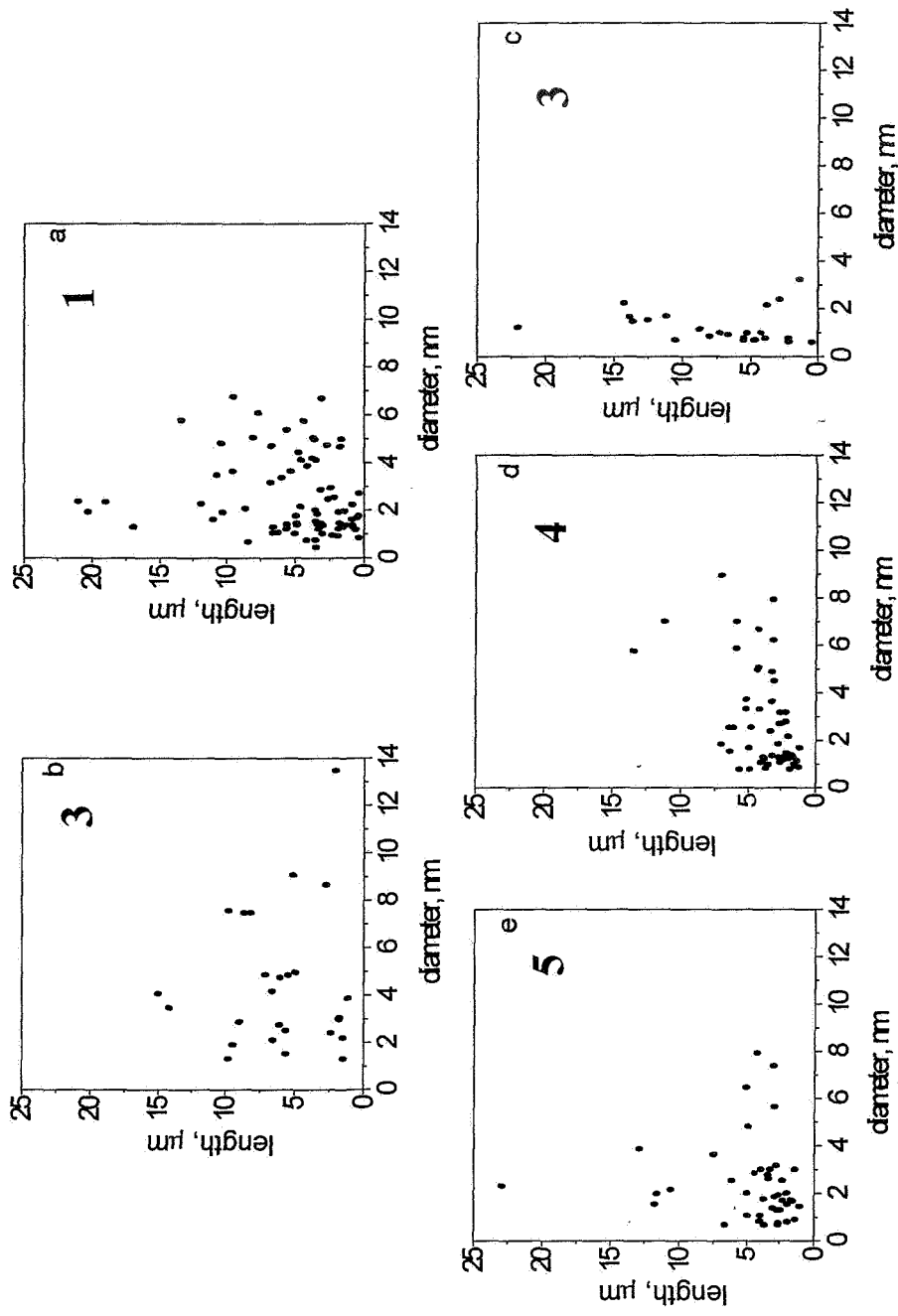
- **SWNT Applications in Composites**
 - Completed a variety of processing techniques for the preparation of composites using thermosets and thermoplastics
 - Characterization of mechanical strength enhancements by DMA, Raman, and tensile tests
 - Utilized polarization study of Raman spectra to deduct load transfer to composites
 - Applied Physics Letters, Vol. 78, pp 3193-3195 (May2001)
 - Completed a study of mechanical response of SWNT ropes under tensile stress: Min. breaking strength of 50 GPa
 - Physical Review Letters, Vol. 84, pp. 5552-5555 (June 2000)







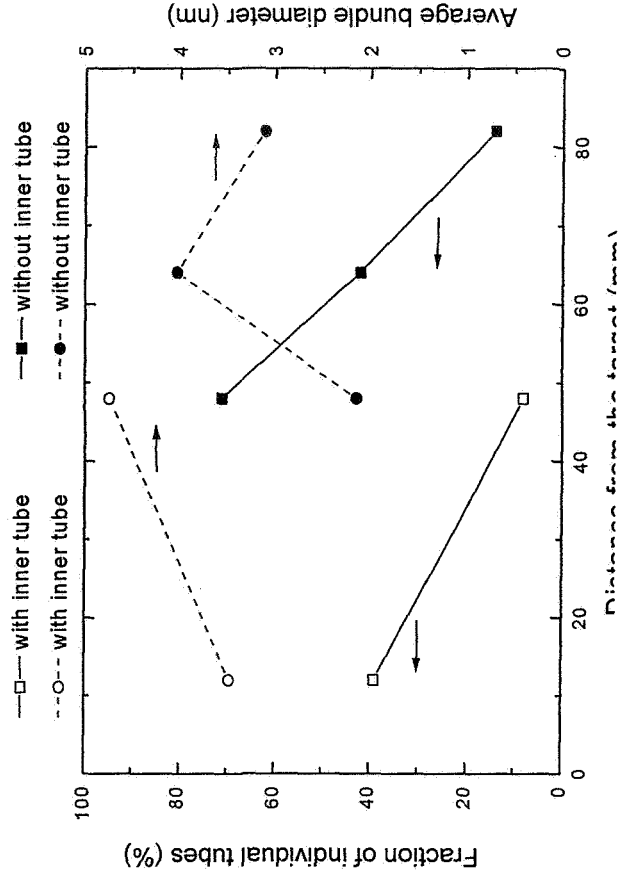
AFM image of plate #1 exposed for 0.5 seconds, with inner tube and argon flowing at 100 sccm. **a)** Individual tube, 1.09 nm diameter. **b)** Individual tube, 1.17 nm diameter, **c)** Thin bundle, 3.28 nm diameter.



• Amount of ropes relative to individual nanotubes and thickness increases farther away from the target (more time to travel, more chance to bundle).

• Ropes and nanotubes deposit farther away from the target without inner tube.

• Relative amount of individual nanotubes is higher without inner tube (plume expands into larger volume, less chance to bundle up)





Purification Methods

- Acid reflux; cross flow filtration; centrifuging; solvent extraction and high temperature annealing
- Solvent Extraction; acid reflux; filtration and centrifuging followed by annealing
- Annealing followed by acid reflux; filtration and centrifuging
- Acid Reflux – Oxidizers like HNO_3 , HCl , HF , H_2O_2

Helped to dissolve metals and amorphous carbon

- Cross Flow Filtration – Surfactants like TritonX

Separated the unbound impurities from pure nanotubes

- Solvent Extraction – Toluene, Benzene, DMF

Dissolved polyaromatics and fullerenes

- High Temperature Annealing in Argon – 500 to 1373 K

Removed volatile components and amorphous carbon

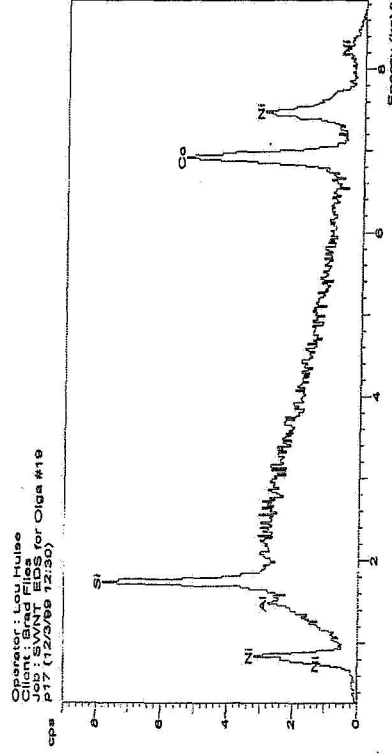
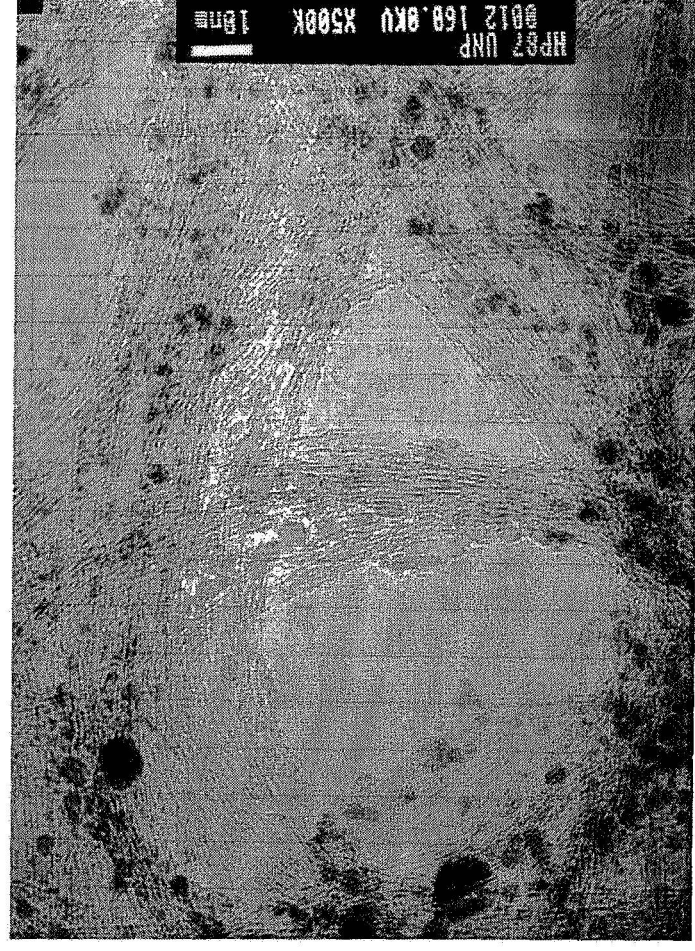
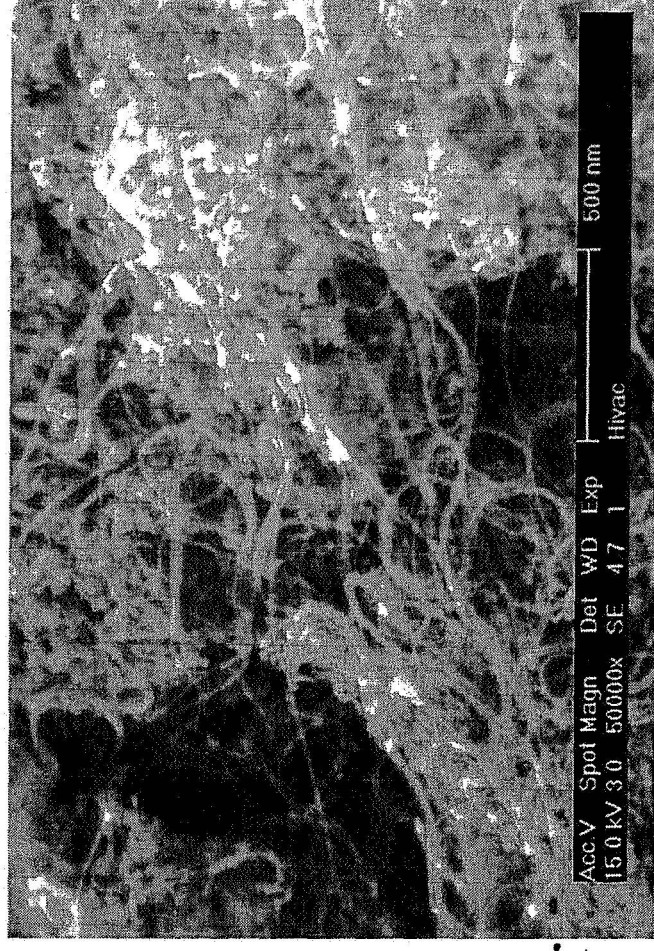


JSC Nanotube Characterization protocol

- **Goal 1:** To gather as much information as possible about specimen purity, metal content, dispersability and homogeneity.
- **Goal 2:** To minimize time and effort spent on characterization.
- **Available tools:** TGA, TEM (+EDS), SEM (+EDS), UV-Vis spectrometry, Raman spectroscopy.
- **We have established a protocol which takes into account known inhomogeneity in nanotube specimens.**
- **Purity information:** TGA, TEM, TEM-EDS, SEM, SEM-EDS, Raman
- **Homogeneity information:** TGA, TEM and SEM to some extent
- **Thermal stability information:** TGA
- **Dispersability information:** Sonication and UV-VIS test

Micro Characterization by Electron Microscopy: SEM and TEM

- **SEM:** Standardized sample mounting. Qualitative elemental analysis with EDX. Rough estimation of purity by comparing image areas.
- **TEM:** Need to wet the sample and dry it on the grid. Diameter distribution (tedious?). Surface imperfections and metallic contaminants. EDX for elemental analysis. Chirality and crystallaneity by electron diffraction.

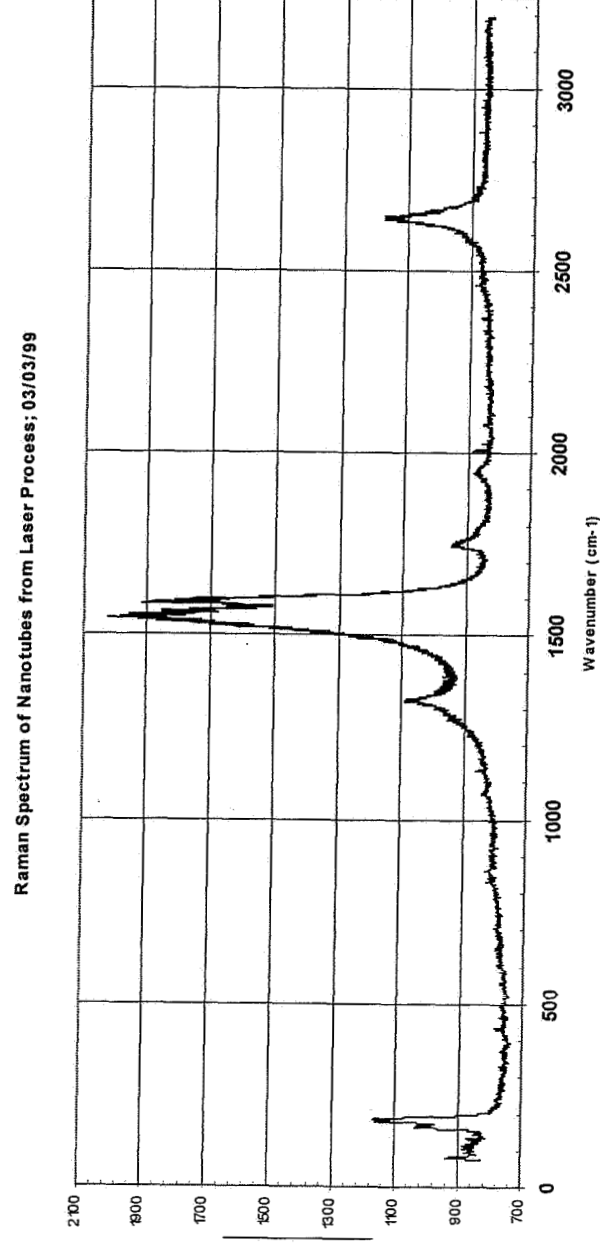
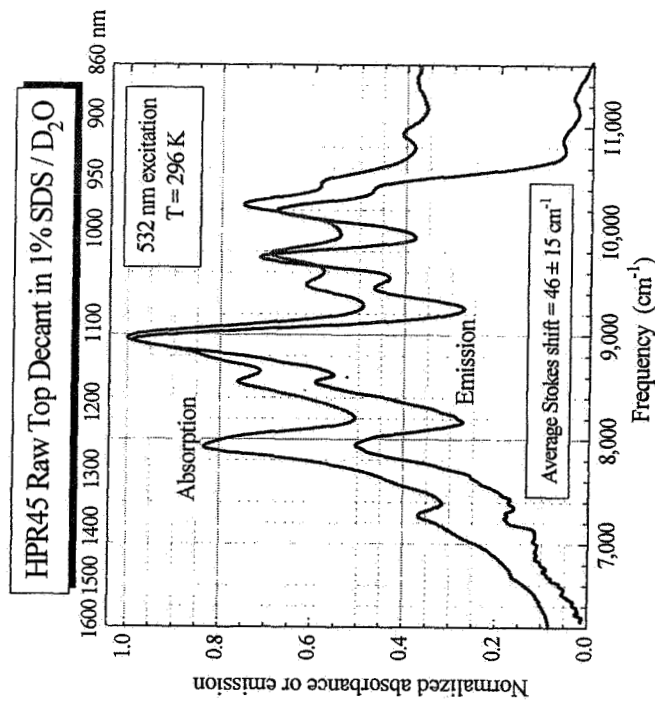
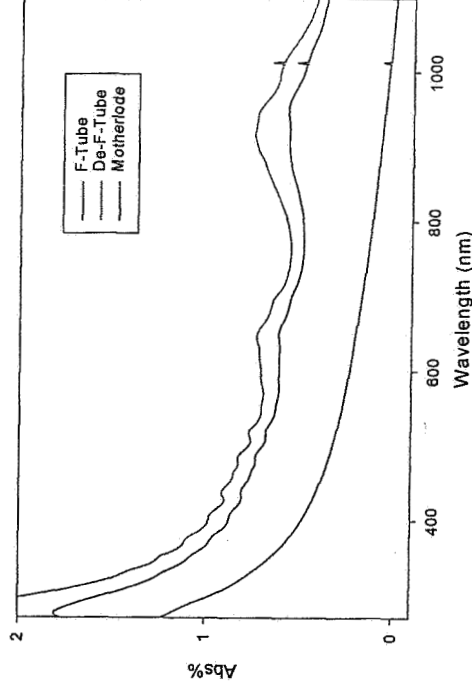


Macro Characterization by Optical Spectroscopy: Absorption (UV-VIS-NIR and IR), Fluorescence and Raman

Absorption: Inter band transitions in UV to NIR regions. Individual tubes vs. bundles. Effects of pH and solvents. Estimation of metals?

Fluorescence: Individual tubes, kinetics in solutions. Metal ligand interactions?

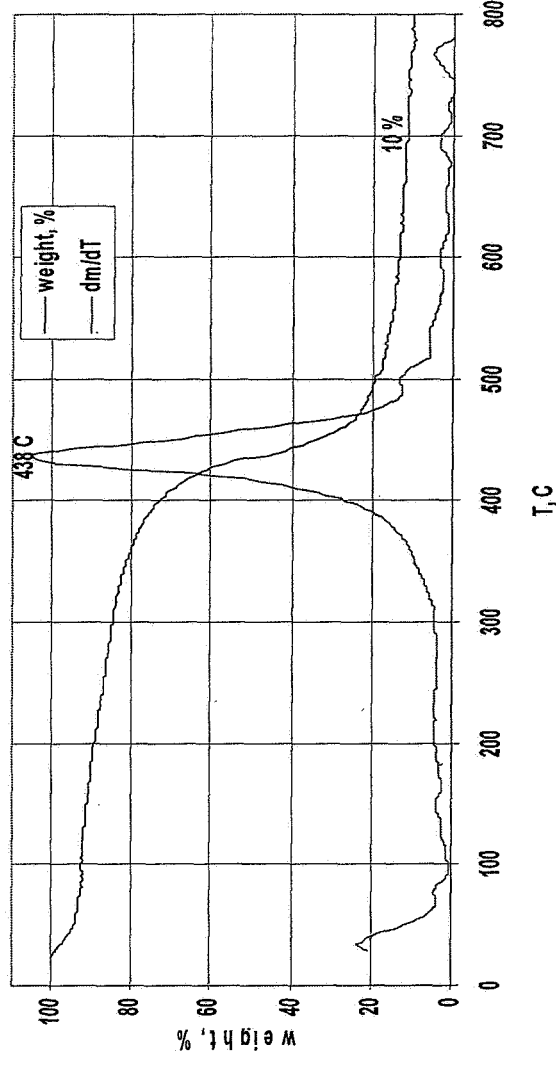
Raman: Small areas (micro?). Diameter distribution. Monitor amorphous carbon.



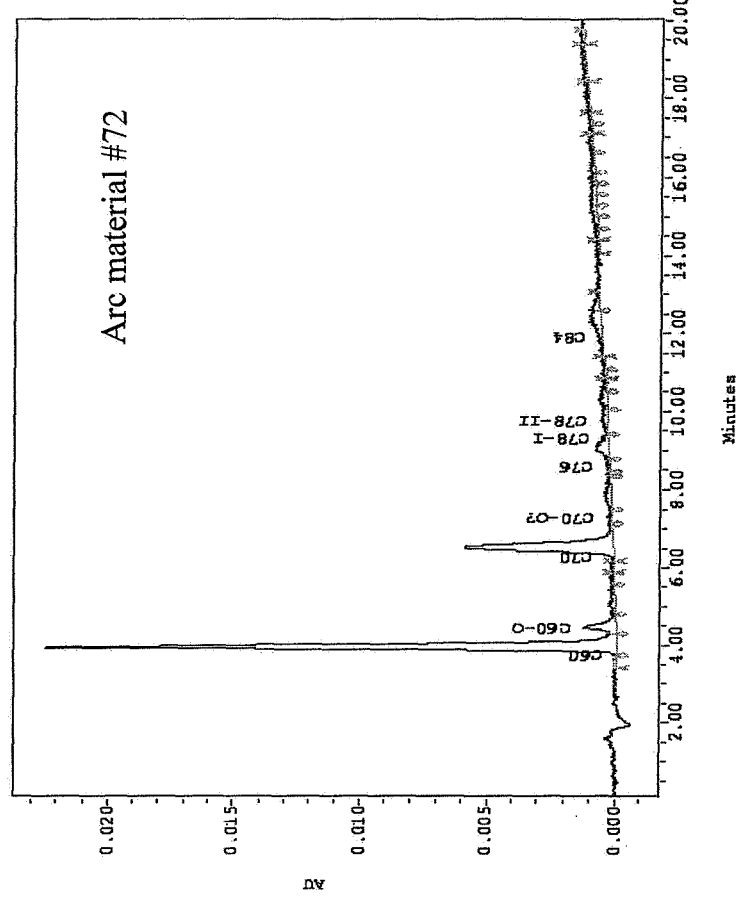
Other Analytical Tools: TGA, AFM, HPLC, NMR, GC-MS, ICP-MS, Microprobe...

- **TGA:** Burning of different types of carbon at different temperatures. Metal content
- **AFM:** Individual tubes vs. bundles. Tube/rope lengths
- **HPLC:** Small liquid samples. Purification tool. Fullerene/hydrocarbon content.

TGA, 8 laser purified



- **NMR:** Hydrocarbon content. Paramagnetic impurities.
- **GC-MS and ICP-MS:** Can be used for carbon and metal contents.
- **Microprobe:** Small areas for metal estimation. Need





How do we go about estimating the purity of SWNTs at NASA-JSC?

- 1. Identify the extent of inhomogeneity.**
- 2. Determine dispersability in selected solvents (DMF, toluene?)**
- 3. Record SEM images.**
- 4. Obtain Raman data.**
- 5. Estimate fullerene and hydrocarbon content.**
- 6. Record TEM images.**
- 7. Estimate non-carbon content by TGA.**
- 8. Identify metals by EDX.**

**NASA-JSC Protocol and Joint NASA / NIST
Workshop**



Composite Fabrication and Testing

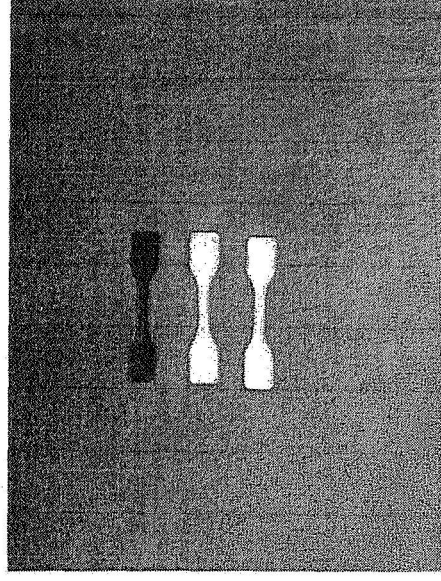
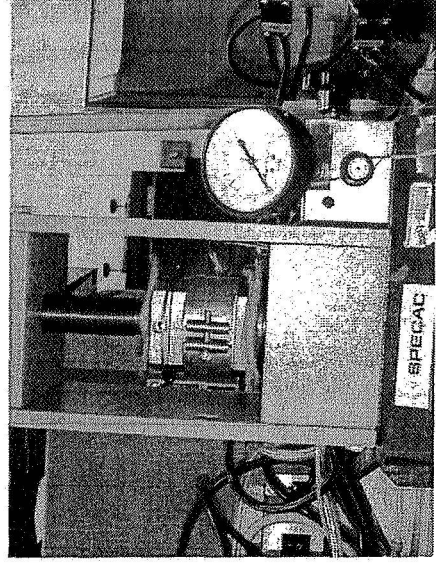
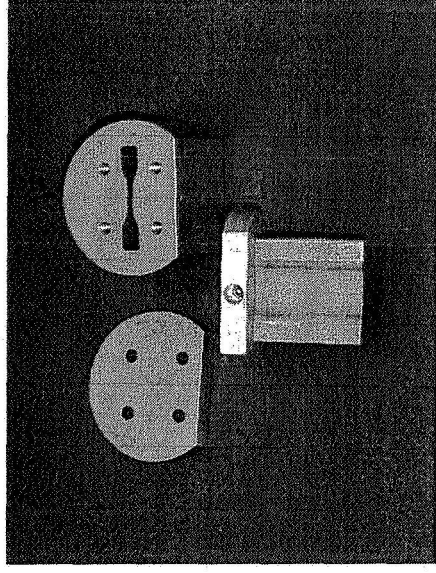
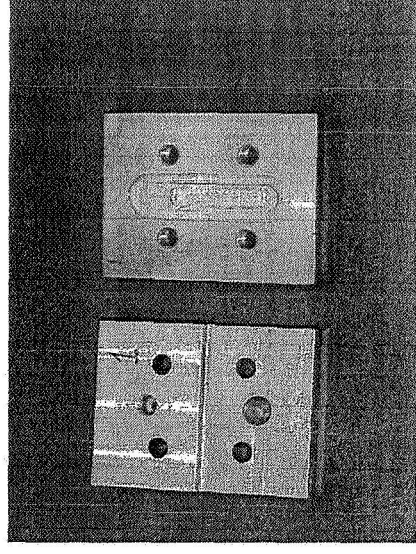
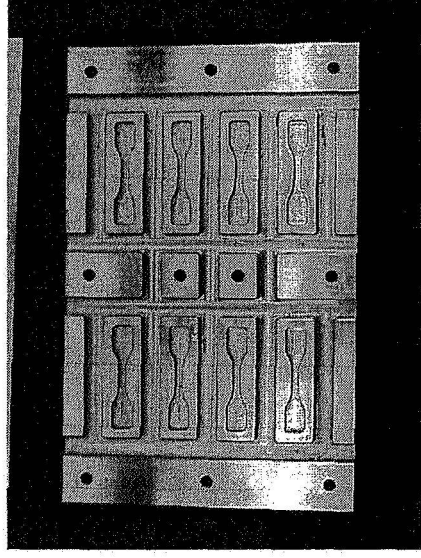
Types: Thermosets, Thermoplastics, Elastomers, Ceramics

Methods: Injection Molding, Casting, Compression Molding, Die Casting and Laminating

Samples: Dog-bone, rectangular samples

Testing: Optical Microscope, Dynamic Mechanical Analysis, Raman, Tensile tests

Characterization: SEM, TEM, and Raman

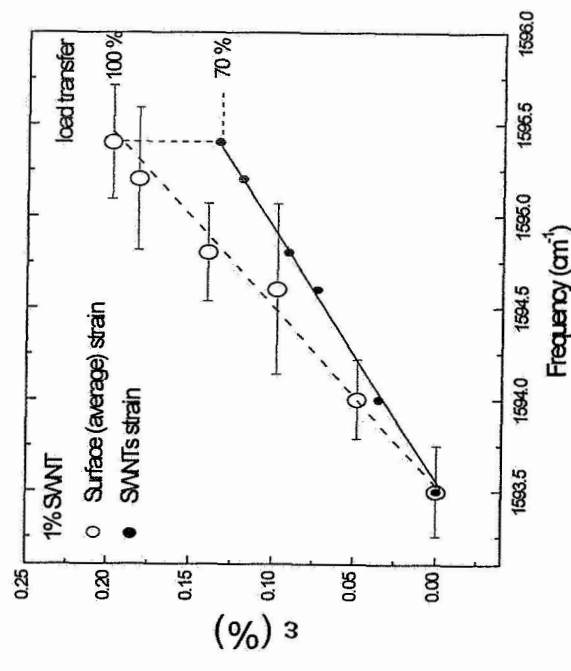
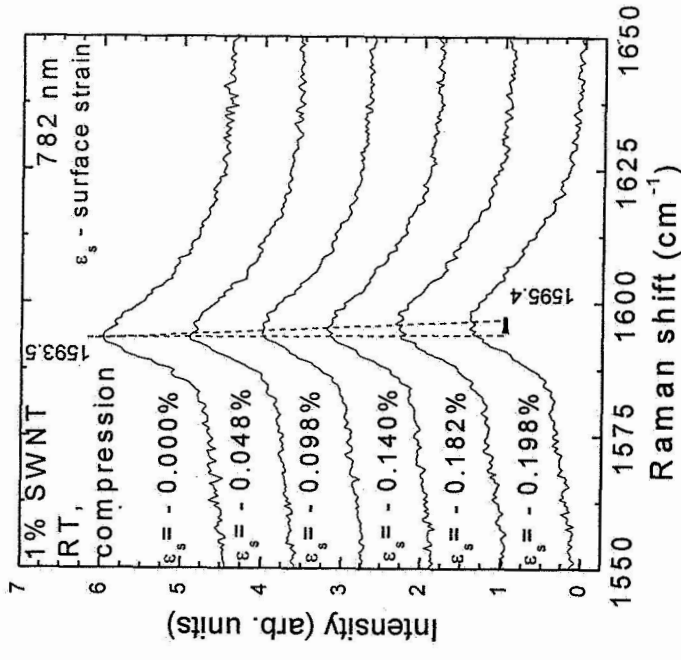
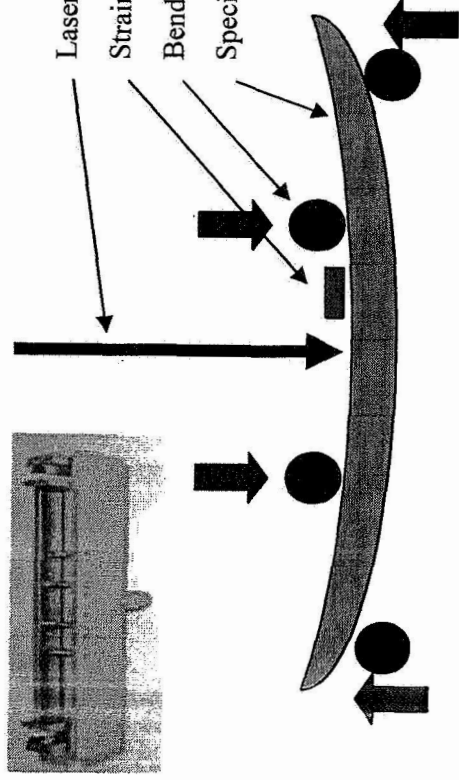




Raman Characterization of Composites

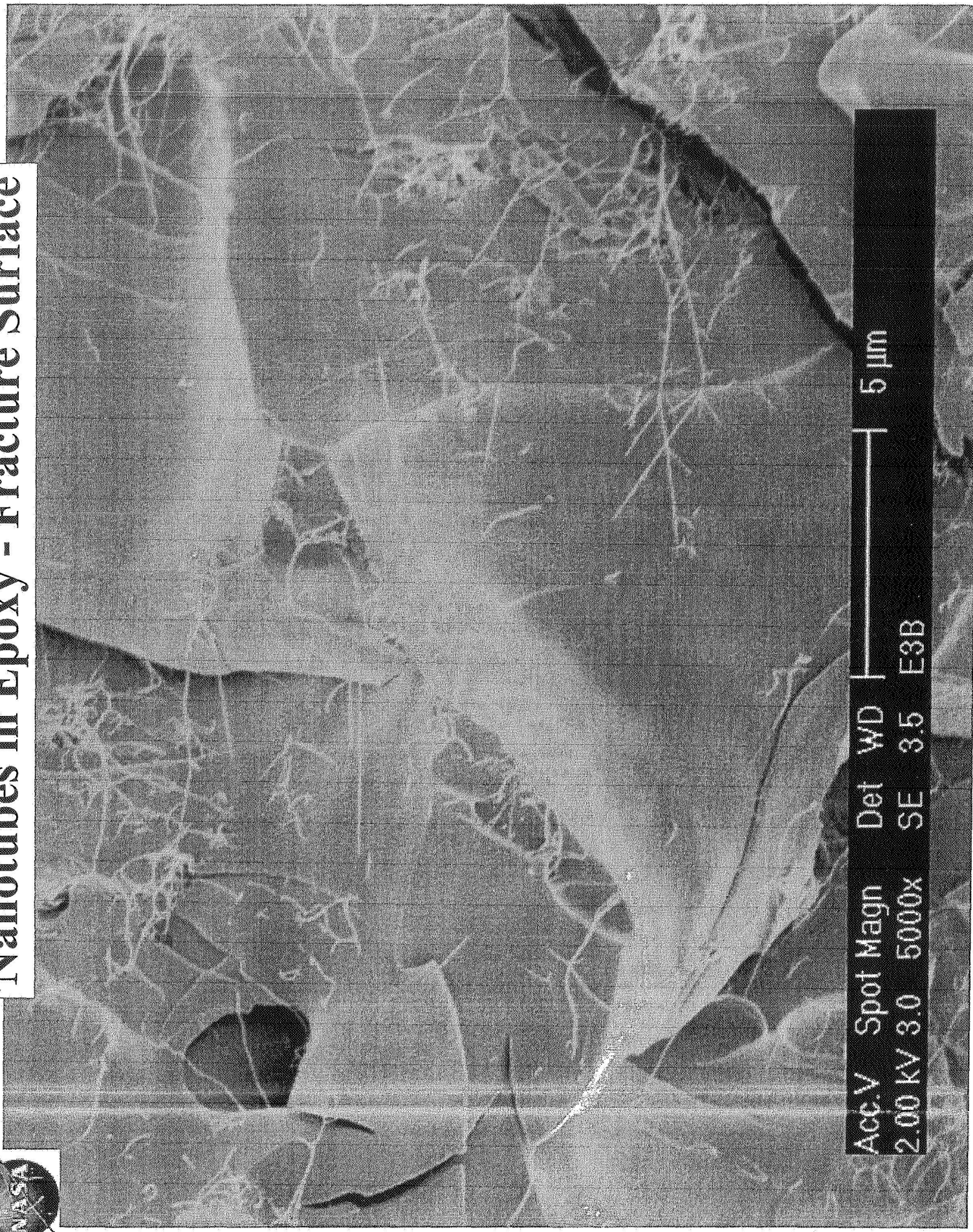
Load Transfer in Nanotube Composites

- **New Tool** - Raman spectroscopy in combination with standard mechanical tests (four point bend) is very useful for testing SWNTs composites.
- Frequency of the tangential mode shifts with applied external compression stress.
- Allows determination of elastic properties of SWNTs/ropes embedded in composite - load transfer.
- **70% Load Transfer** (1%SWNT in epoxy)





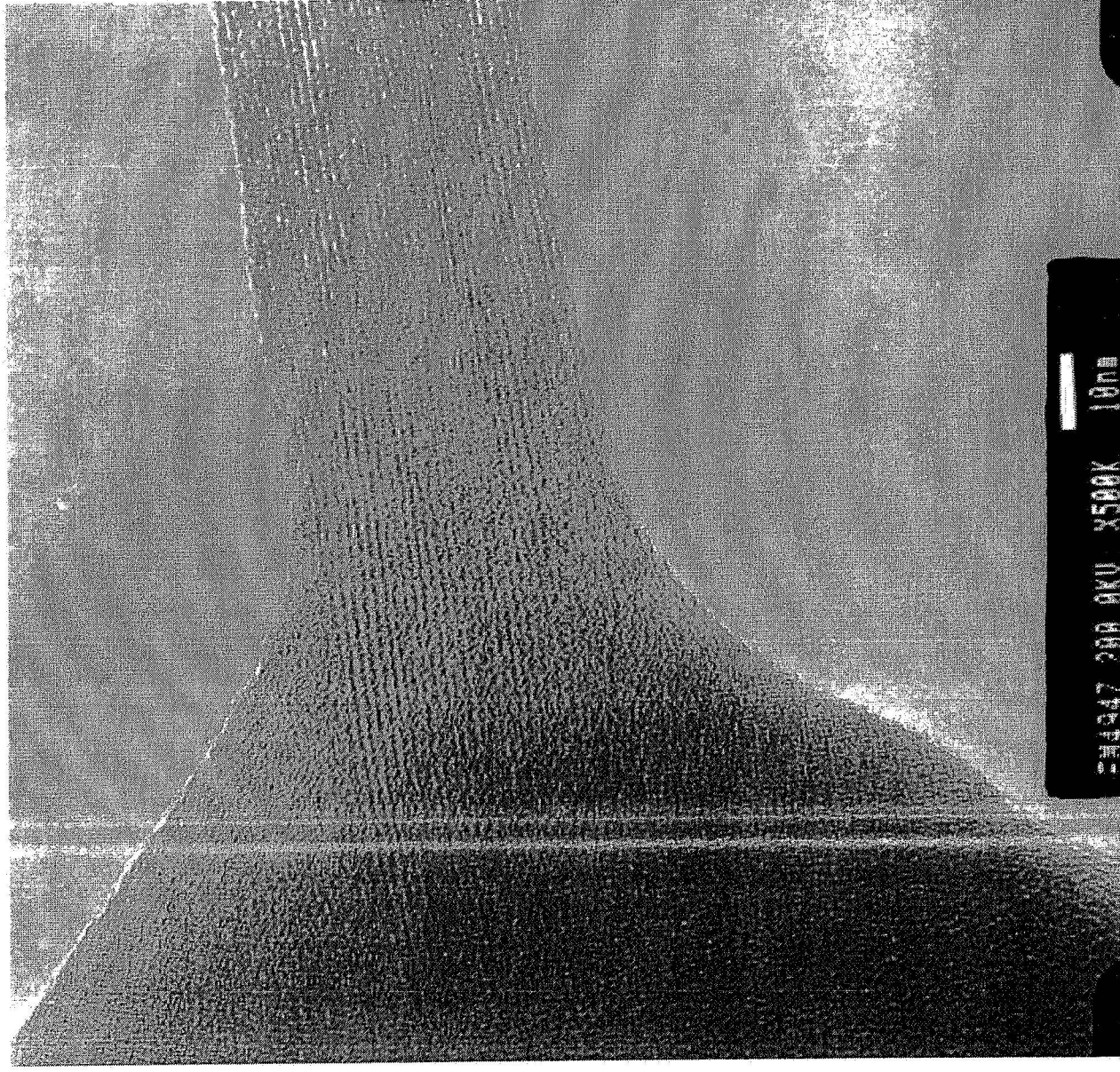
Nanotubes in Epoxy - Fracture Surface



Acc.V	Spot	Magn	Det	WD	5 μ m
2.00 kV	3.0	5000x	SE	3.5	E3B



Excellent Wetting of Nanotube Bundle in Epoxy



Why no big increase in strength?

- Bundles too large
- Curvature too high
- Wetting vs. bonding



Future Nanotube work at NASA-JSC

- 1. Modify laser production for improved yield.**
- 2. Modify purification procedures to include variability of initial soft bake temperatures with samples.**
- 3. Expand the JSC protocol to include optical microscopy for dispersion and TPO for identifying different types of carbon.**
- 4. Establish techniques to monitor amorphous carbon.**
- 5. Improve derivatization techniques to for selectivity of functional groups, their location and extent.**
- 6. Improve methods to produce selective individual tubes and to disperse SWNT bundles.**
- 7. Continue work on nanocomposites for mechanical, electrical and thermal aerospace applications.**



Government Collaborations

NASA Glenn Research Center

- Functionalization, purification, high temp. mat'ls (Meador, Gray)

NASA Ames Research Center

- Nanotubes (JSC) / modeling of HiPco (Meyyappan, Srivastava)

NASA Langley Research Center

- Code R 8 – Production/purification (JSC) for use in SWNT composites (Siochi, Sutter)

NASA Marshall Space Flt Center

- Nanotubes, MMCs (Gill, Hudson)

Air Force Research Lab.

- Composites, characterization, purification (Maruyama)

Naval Research Lab.

- Composites (Imam)

Nat'l Renewable Energy Lab

- Purification (Heben, Dillon)

Oak Ridge Nat'l Lab.

- Thermal characterization (Wang Dinwiddie)

NASA Glenn DoD - AFRL

NASA Ames DoD - NRL

NASA Langley

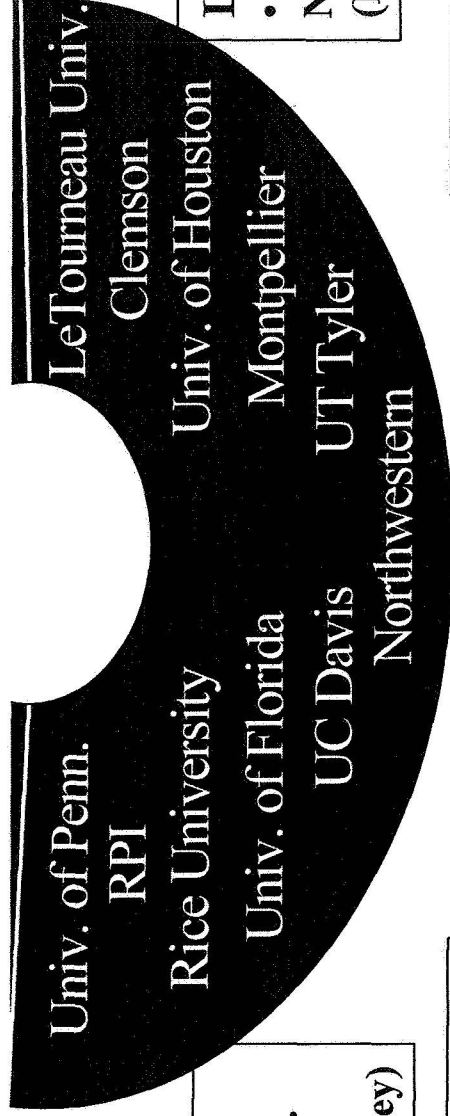
NASA Marshall

DoE - NREL

DoE - ORNL



University Collaborations



Univ. of Pennsylvania

- CDDF - Thermal Mgmt. Mat'ls (Fischer)
- Composites (Luzzi, Winey)

Rensselaer (RPI)

- Composites (Schadler)

Rice University

- Cooperative Agreement – Advanced Nanotechnology Mat'ls and Applications Yr. 4/5 (Smalley, Tour, Barrera, Margrave)
- Computational Mat'ls Sci. (Yakobson)
- Nanoshells (Halas)

University of Florida

- Isolated SWNTs (Rinzler)

Univ. of Calif. - Davis

- Nanocrystalline Ceramics (Mukherjee)

Northwestern

- Mechanics/composites (Brinson)
- Nanotubes (Ruoff)

Clemson University

- Isolated SWNTS - STM (Carroll)

University of Houston

- ISSO, year 3 of 3 – Raman Characterization (Iliev, Hadjiev)
- GSRP, year 1 of 2 – Polymer chem., dispersion, composites (Mitchell, Krishnamoorti)

Univ. of Montpellier

- Arc process (Bernier)

Univ. of Texas - Tyler

- Summer Faculty Fellow - CFD of Laser process (Greendyke)

LeTourneau Univ.

- Summer Faculty Fellow Nanotube growth process (DeBoer)



Team Members

Dr. Sivaram Arepalli
Dr. Rodrigo Devivar
Dr. Brad Files
Dr. Olga Gorelik
Dr. Brian Mayeaux
Dr. Pavel Nikolaev
Dr. Carl Scott
Dr. Erica Sullivan
Dr. Leonard Yowell



Mr. William Holmes
Mr. Lou Hulse
Mr. Jeremy Jacobs
Ms. Beatrice Santos

<http://mmptdpublic.jsc.nasa.gov/jsenano/>

ACKNOWLEDGMENTS

- Dr. Rick Smalley and Dr. Bob Hauge of Rice University
- Dr. Victor Hadjiev of Univ. of Houston
- NASA-JSC Director's Discretionary Funds
- Lockheed Martin ETAC contract



Carbon Nanotube Activities at **NASA/JSC**

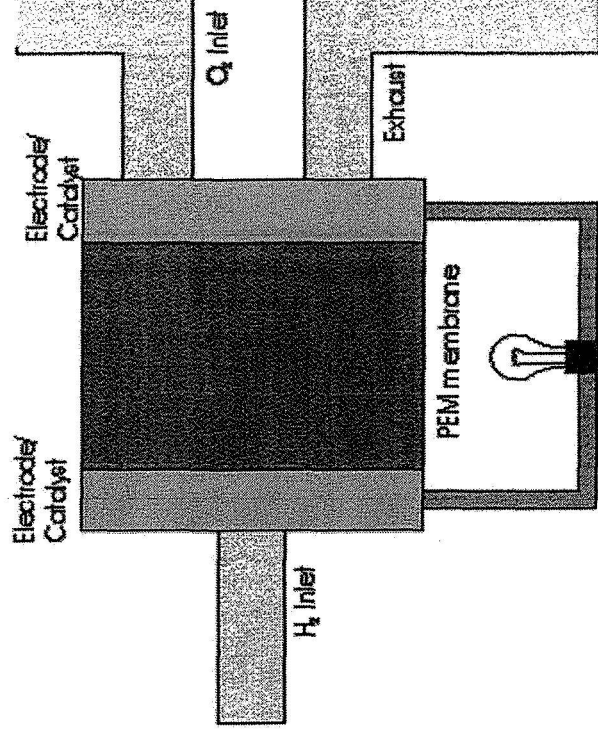
Sivaram Arepalli

Thanks for your time!

Will be happy to answer a few questions!

Proton Exchange Membrane

- Hydrogen and oxygen are oxidized and reduced at the electrodes
- e^- flow externally to create a current
- H^+ transverse the membrane.
- All recombine at the cathode to create water



Requirements a PEM Fuel Cell

Electrodes

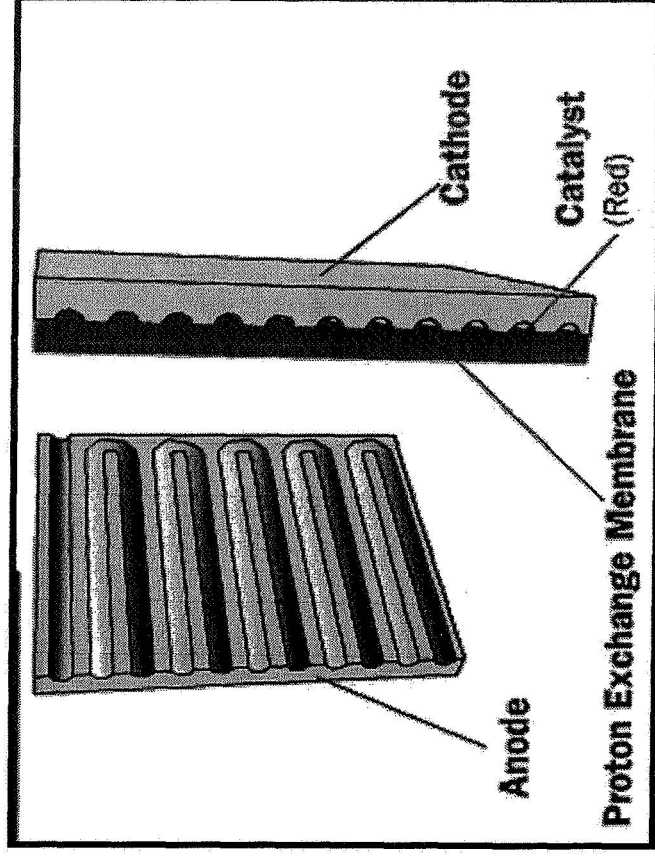
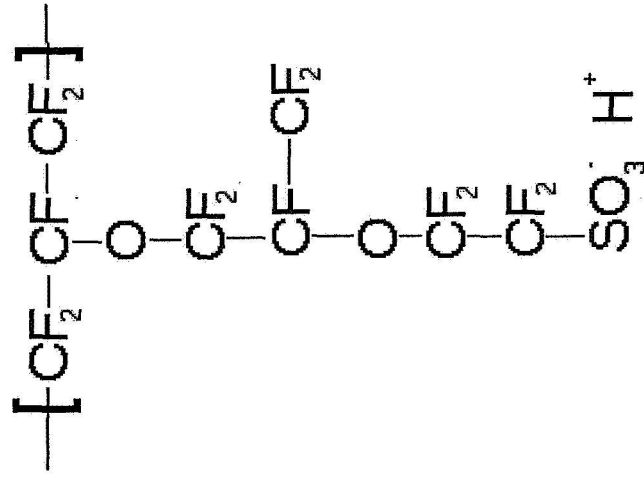
- Electrodes must be conductive
- Electrodes should have high surface area
- Electrodes must be permeable to O_2 and H_2 .

Membranes

- Membrane must be an insulator (electrical).
- Membrane must be permeable to H^+ .
- Membrane must be impermeable to O_2 and H_2 .

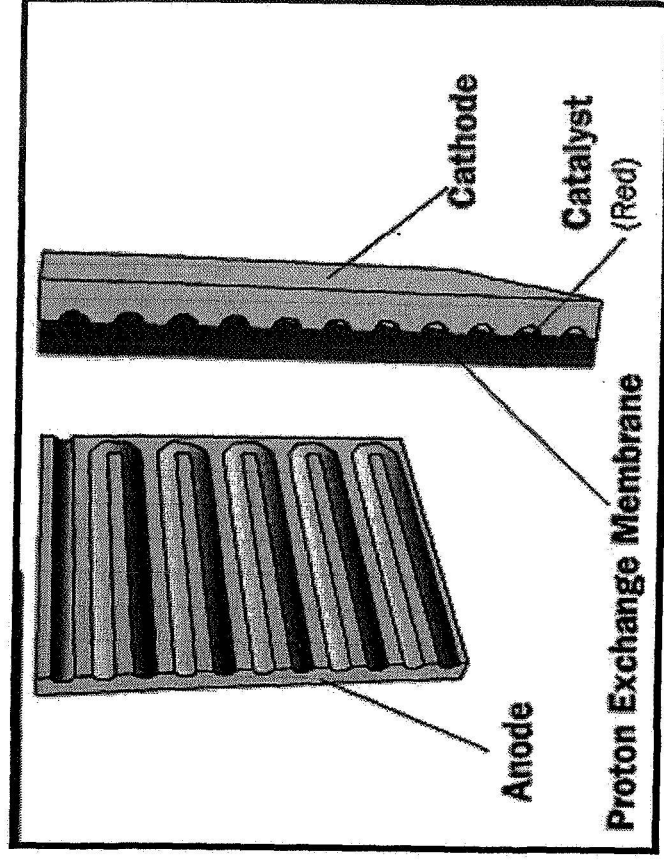
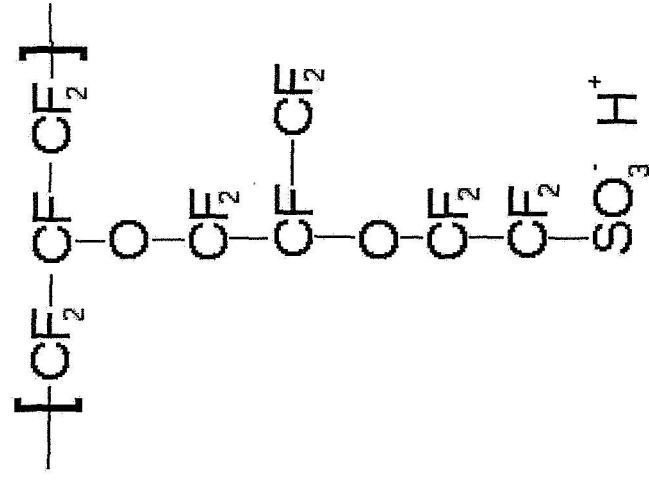
Membrane and Electrodes

- Electrodes have been made from slurry of carbon black and Pt black.
- To date, the membrane of choice is 3M's Nafion.



Membrane and Electrodes

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SWNT for Fuel Cells

As Electrodes

- SWNT are conductive.
- SWNT have high surface area.
- SWNT have longer conductive path than carbon black.
- H₂ mobility along the tube would be higher, possibly reducing the necessary Pt loading.

As Membranes

- Side walls of SWNT would have to be derivatized to become insulating.
- Derivatized SWNT are soluble in ordinary organic solvents.
- Negative charge would be delocalized so H⁺ removal would be enhanced.

Schedule of Work

Electrodes

- Make electrodes by filtration from low surface tension suspensions.
- Bake under inert atmosphere.
- Test surface area with BET surface analyzer
- Test electrical conductivity
- Test O₂ and H₂ diffusion
- Impregnate with Pt salt and reduce in oven.

Membranes

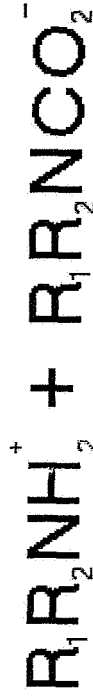
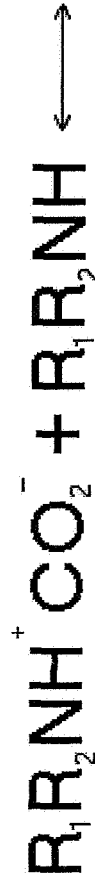
- Derivatize (F₂ or oleum) SWNT
- Suspend DSWNT in organic solvent
- Make membranes
 - Filter from suspensions
 - Evaporate on PTFE
 - Dry with heat/pressure
- Test electrical resistance across membrane
- Test for O₂ and H₂ diffusion
- Insert into standard fuel cell

RCCRS - Regenerable CO₂ Removal Systems

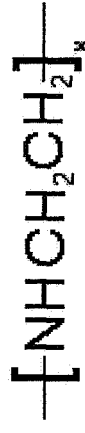
- Plastic beads are coated with an amine
- Beads are packed in a compartment
- CO₂ reacts with amine and is retained in the chamber
- Applying vacuum and heating reverses the reaction, removing CO₂

Heat Exchange Problems with Current System

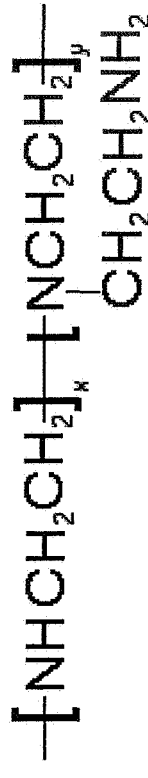
The reaction of Polyethylenimine with CO_2 is exothermic. During CO_2 removal, the system heats up, this reduces the efficiency of CO_2 removal from the atmosphere.



Polyethylenimine



Linear

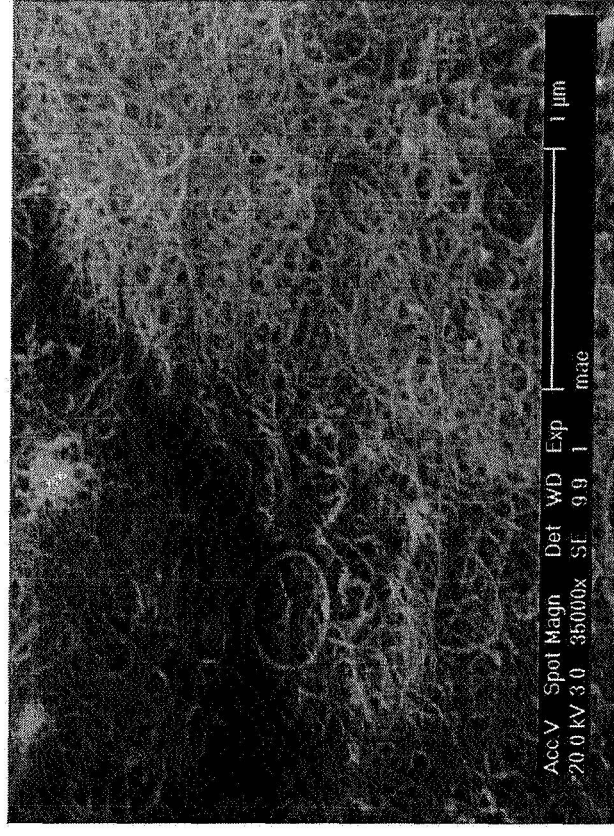


Branched

The reverse reaction is endothermic, which cools the system. Again efficiency of CO_2 removal is reduced. This time, the removal is from the amine substrate.

Thermal Transport is the Key to Efficient CO₂ Removal

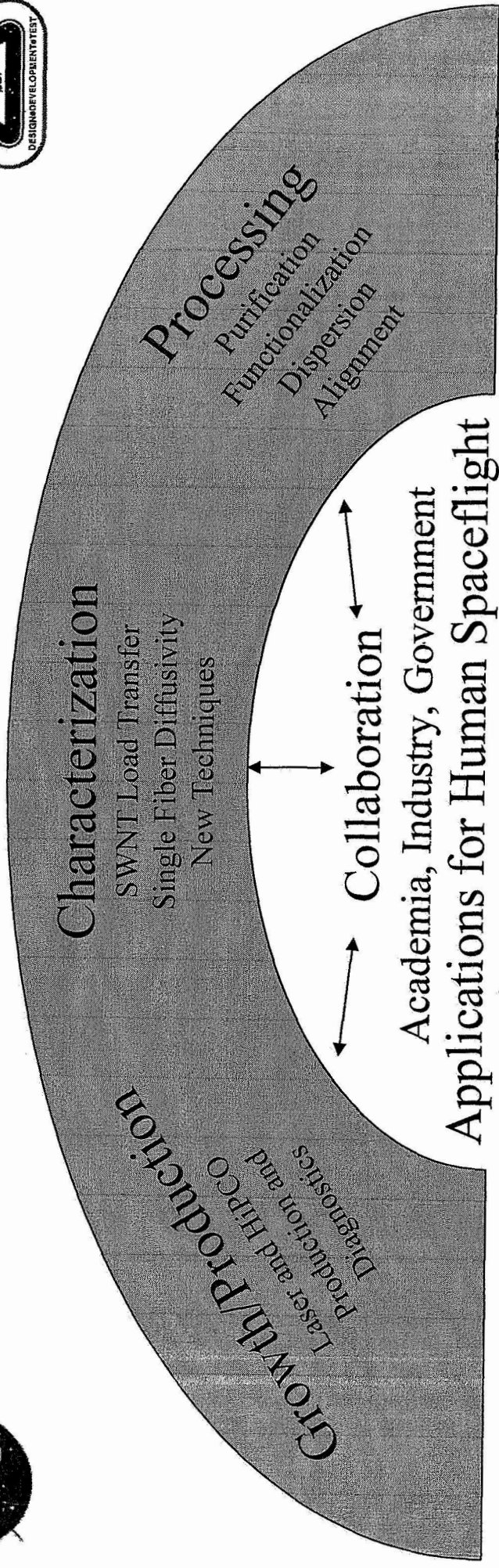
- Nanotubes have a thermal conductance comparable to diamond along the axis.
- Nanotubes have large surface areas.
- Amines have been used to “hold” nanotubes to surfaces; i.e. amines stick to nanotubes.



- Multiwall nanotubes are available in large quantities.
- Multiwall nanotubes can be catalytically grown on multiple surfaces including meshes.



Nanoscale Materials and Processes



SUPPORT	APPLICATION	PARTNERS					TRL				
		1	2	3	4	5	1	2	3	4	5
SBIR Phase II	Ultracapacitors	EP, Glenn					X	X	X	X	X
Rice (NCC 977)	Electrostatic Discharge Materials with Nanotubes	Rice, LaRC					X	X	X		
None	Proton Exchange Membrane- PEM - Fuel Cells	EP, Glenn					X	X			
CDDF-ES	Nanotube-Based Structural Composites	Rice, UH, LaRC					X	X			
None	RCCRS - Regenerable CO ₂ Removal System	EC, Ames					X				
CDDF-ES	Ceramic Nanofibers for Thermal Protection Materials	ES3, Ames, Glenn, USAF					X				
SBIR Phase I CDDF-ES	High Thermal Conductivity Fabric for Spacesuits	EC, Rice, ORNL					X				
CDDF-NX	Radiation Resistance/Protection	NX, Rice, PV, LaRC, Ames					X				
None	Active Thermal Control Systems for Space	EC					X				
CDDF-ES	Nanoshells for Thermal Control Coatings	ES3, Nanospectra					X				



What should we know about the Purity of the material?

Production Method and Source: Arc, CVD, HiPco, Laser,

Physical Appearance: Color, form, weight, homogeneity,

Solubility: Water, methanol, acetone, toluene, DMF, CS₂,

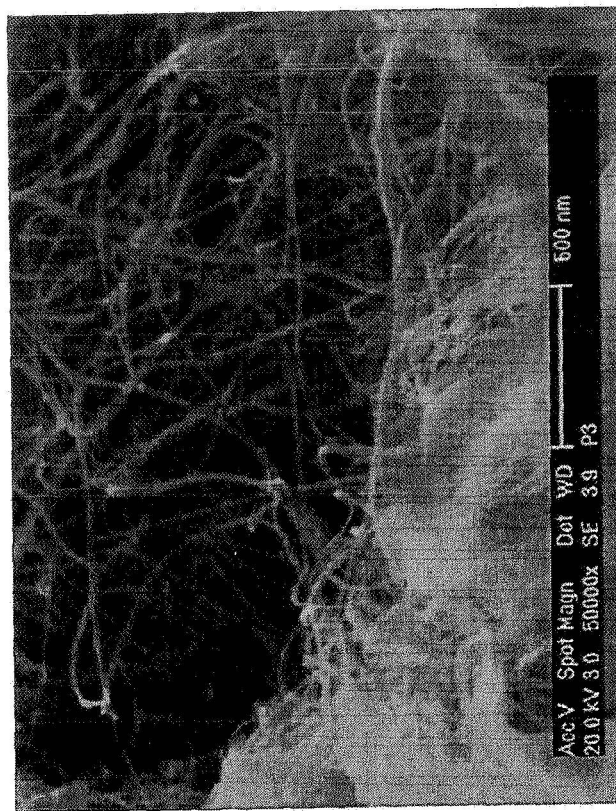
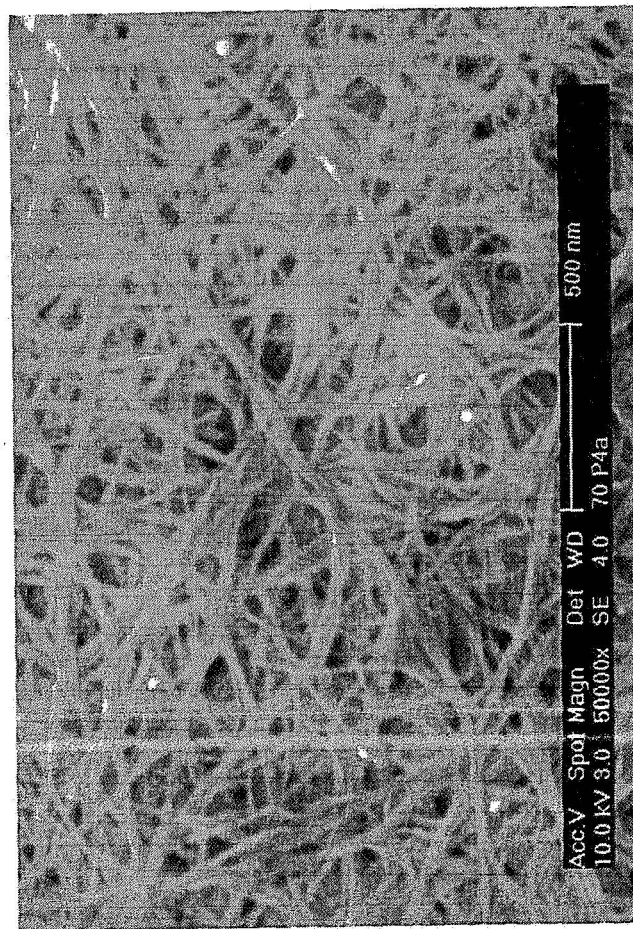
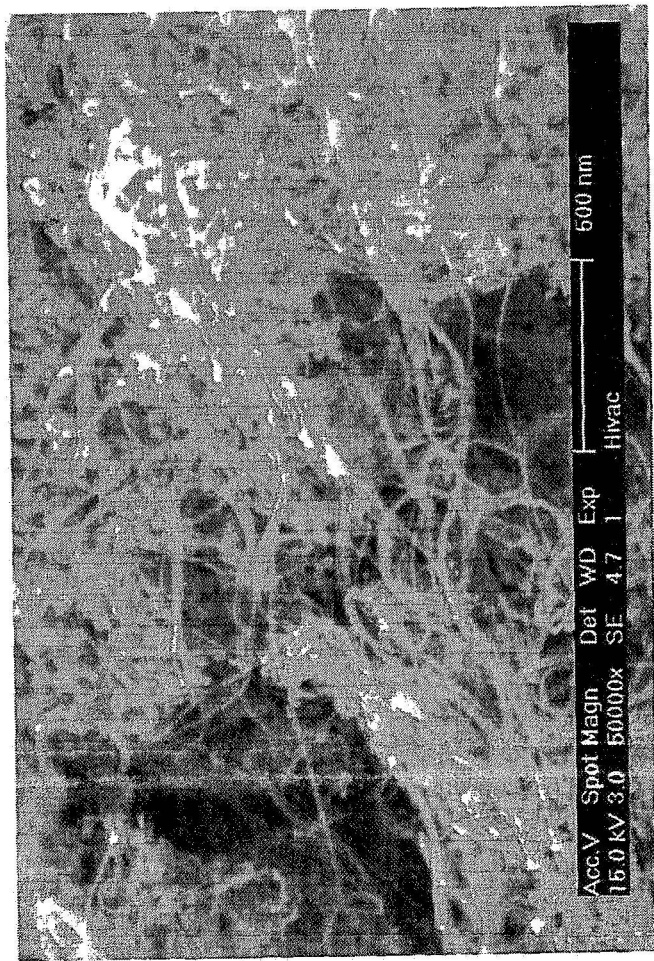
-- Suspension, Flotation, Flocculation

Dispersability: Visible transmission and changes with time

Electron Microscopy: SEM, TEM, EDX, XPS,

Spectroscopy: UV-VIS-NIR and IR absorption, Fluorescence and Raman

Other Analytical Tools: AFM, HPLC, NMR, GC-MS, Microprobe,



Considering Basic Composites Analysis

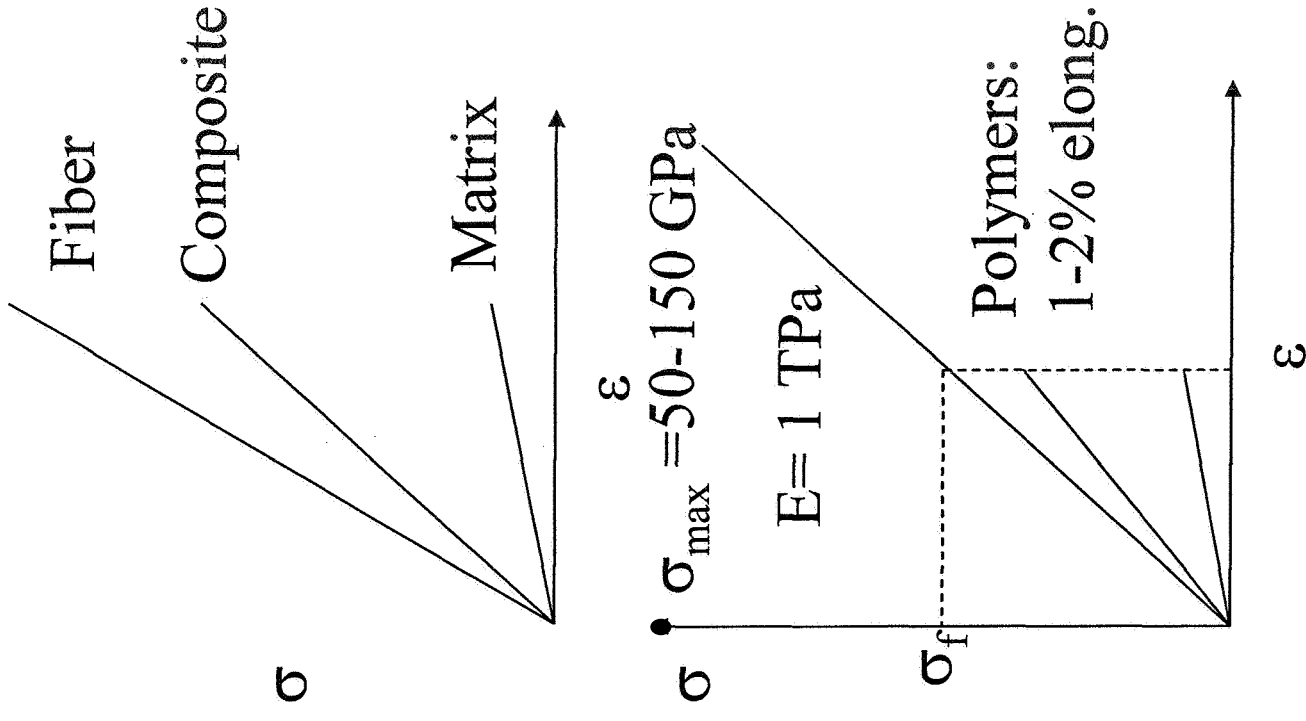
Typical composites construction based on the volume fraction rule.

Note similarities in strain to failure. Usually the matrix fails after the fiber.

However, Nanotubes have 5% elongation to failure.

Composite approaches throw away a significant contribution from the nanotubes.

Analysis with this approach would produce a material with a 3000% increase in *strength, assuming ideal bonding and 1-D reinforcement.



Quick Calculation

Stiffness of SWNTs, $E = 1 \times 10^{12}$ Pa

$E = \text{stress/strain}$

If failure strain = 5%, failure stress = $1 \times 10^{12} \times 0.05$
= 50 GPa

If material fails at 1%, stress in fibers = 10 GPa

Correction for 3-D randomness, $1/9 \times 10 \text{ GPa} (\sim 1 \text{ GPa})$

If material has 1% SWNTs, $0.01 \times 1 \text{ GPa} = 10 \text{ Mpa}$

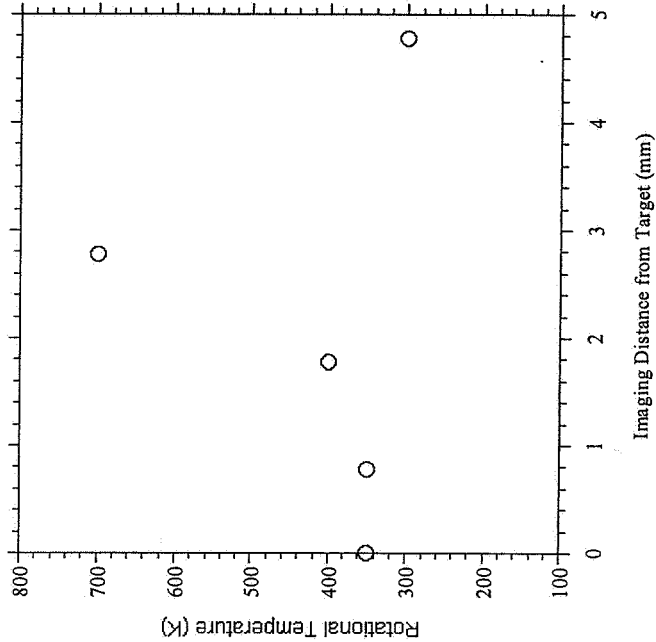
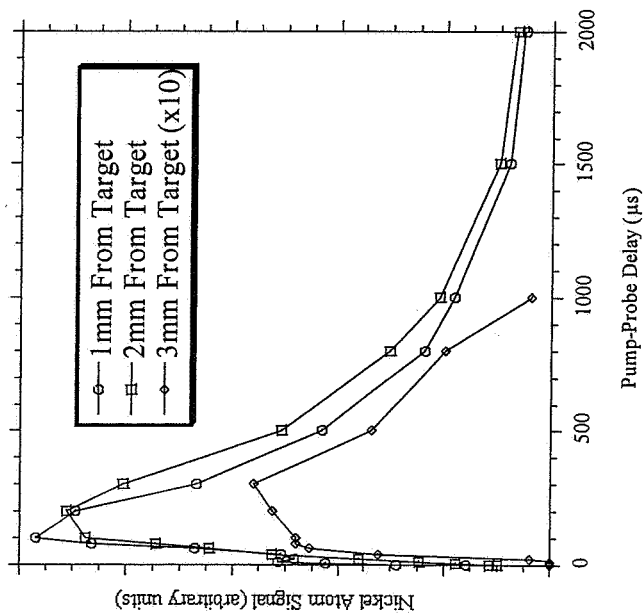
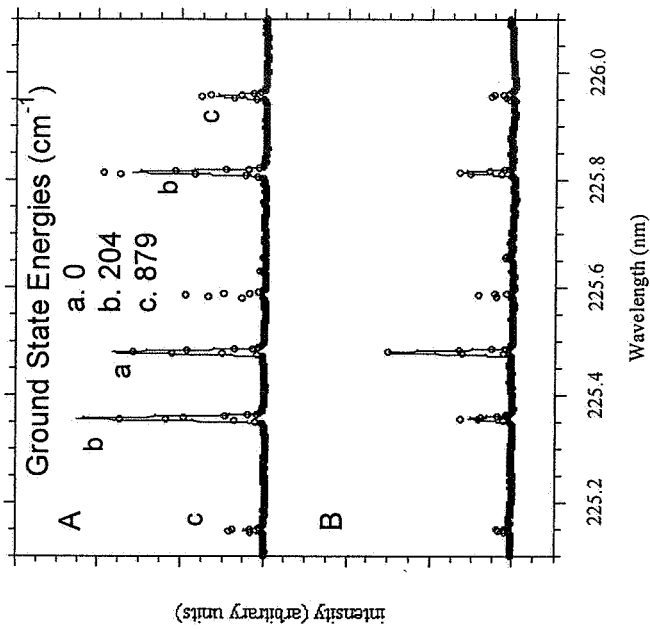
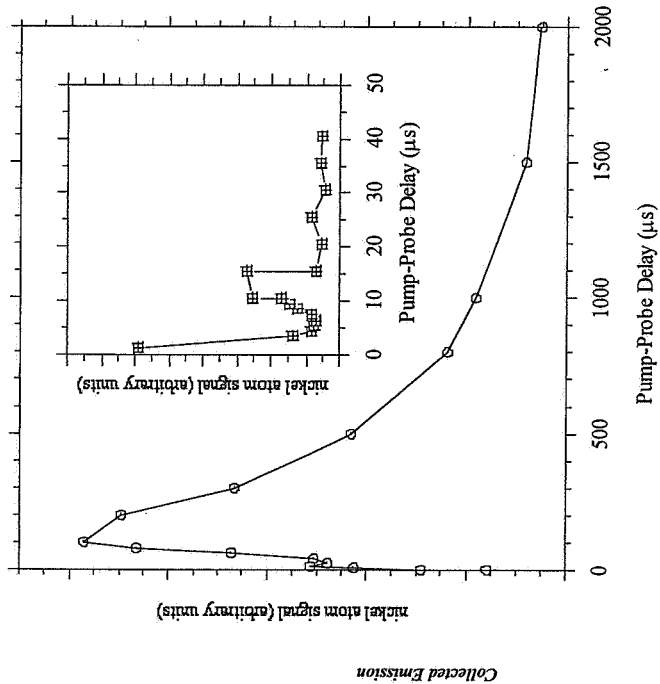
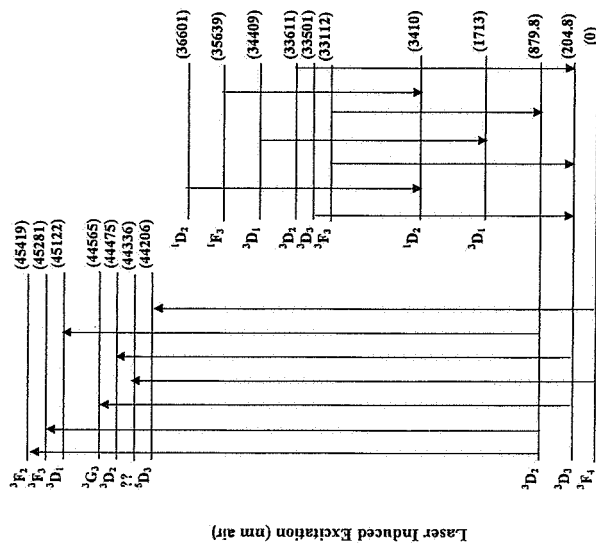
Epoxy tensile strength is 76 Mpa

Rule of Mixtures $10 \text{ MPa} + 76 \text{ Mpa} = 86 \text{ MPa}$

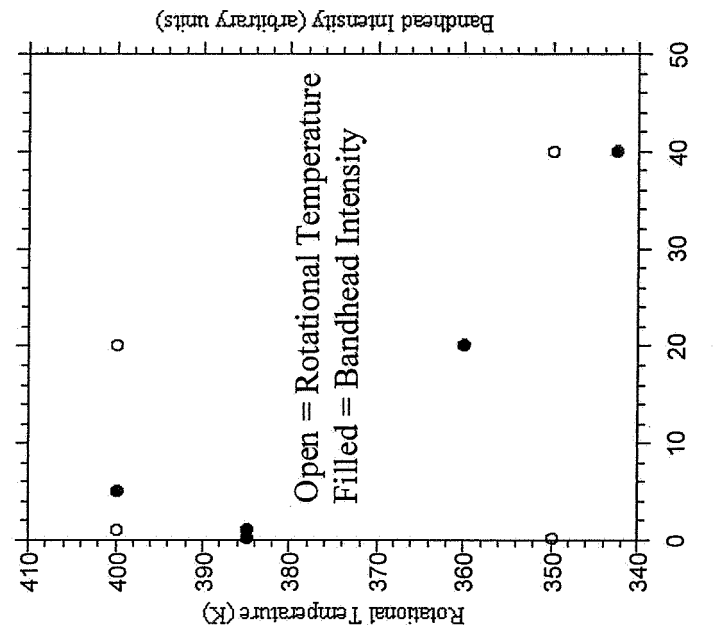
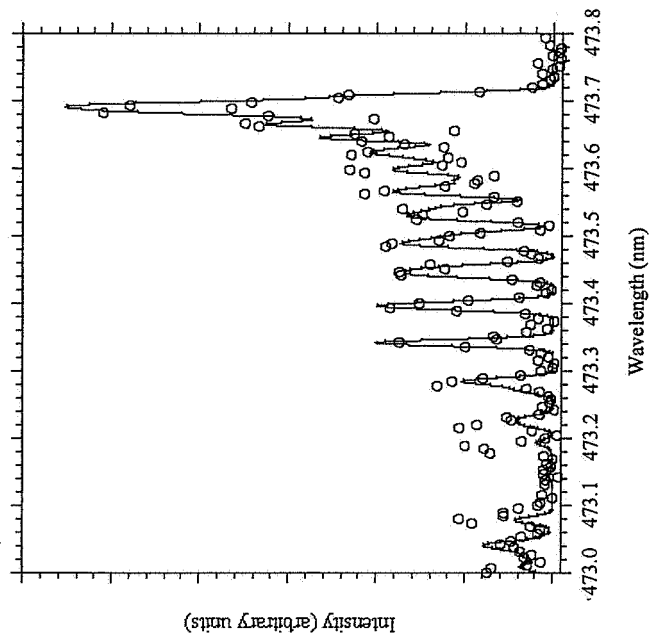
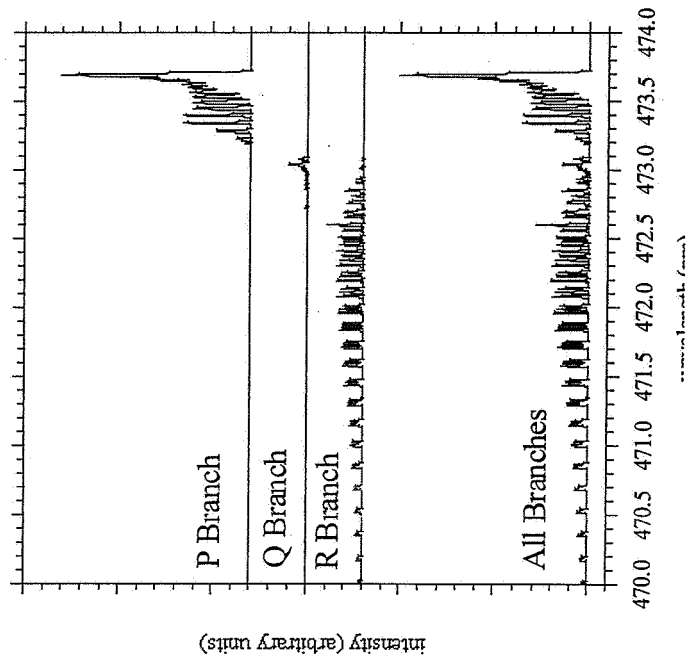
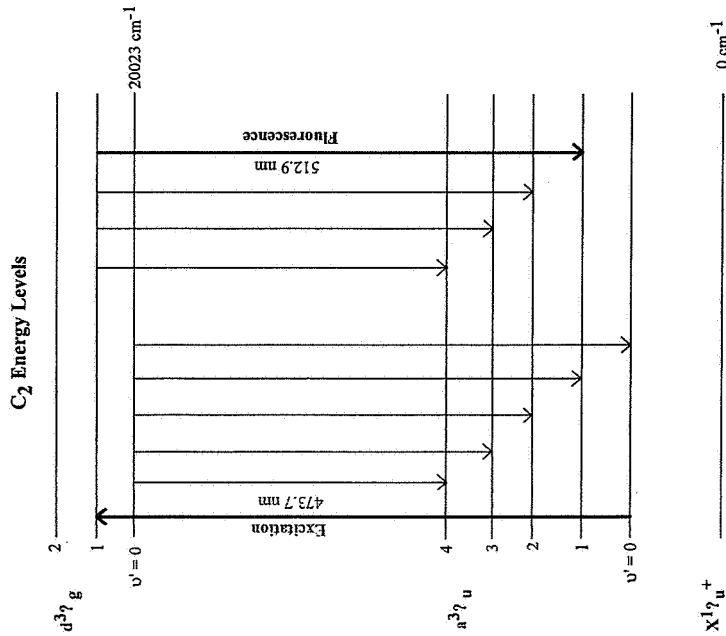
Dispersion

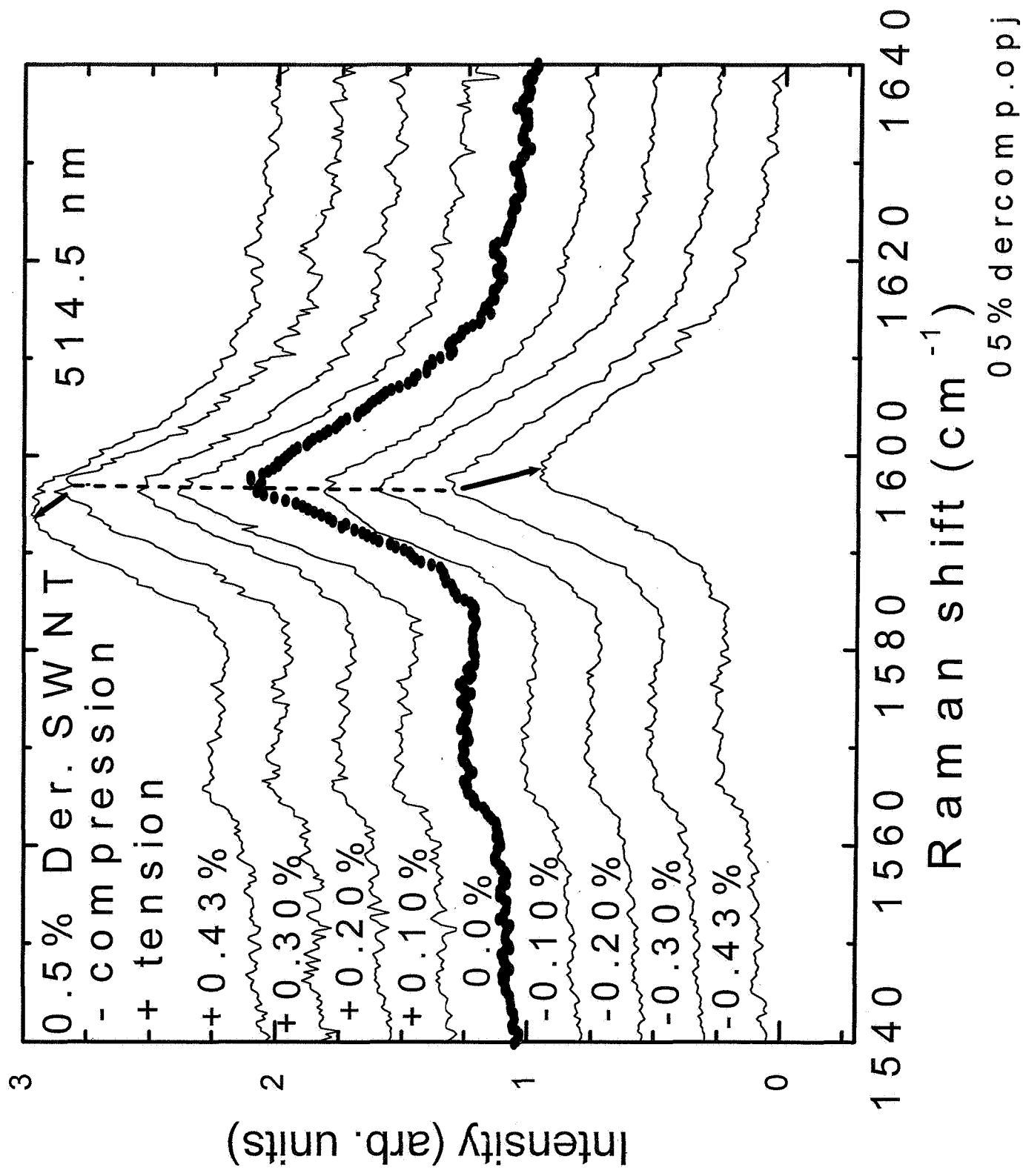
- Both dispersion of ropes and individual tubes of SWNTs and epoxy
- Study compatibility with solvents
- Currently use acetone/toluene mixture for epoxy work
 - Toluene is used for compatibility with resin
 - Acetone is used to reduce evaporation time
- Need method to characterize dispersion
 - Light transmission, UV/VIS, Optical microscopy?
- Try water-soluble resins with wrapped tubes
- Work with surfactants?

LIF of Nickel Atoms in Plume



LIF of C₂ in Plume





0.5% SWNT composite

